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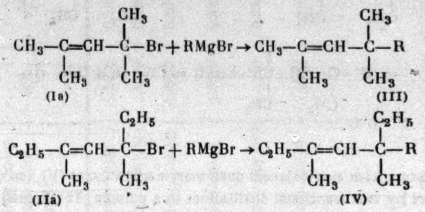
SYNTHESIS OF HYDROCARBONS

LXVI. C_{11}-C_{16} HYDROCARBONS WITH TWO ADJACENT QUATERNARY CARBON ATOMS

R. Ia. Levina, P. A. Kaikaris, A. V. Simolin, and E. G. Treshchova

In our preceding communications [1,2] we described the reaction between alkyl magnesium bromides and tertiary bromides of the allyl type as a method of synthesis of alkenes containing one quaternary carbon atom (III and IV). The tertiary allyl bromides used were 2-bromo-2,4-dimethyl-3-pentene (Ia; hydrobromide of 2,4-dimethyl-1,3-pentadiene) [1] and 3-bromo-3,5-dimethyl-4-heptene (IIa, prepared by hydrobromination of a mixture of two isomeric dienic hydrocarbons with the same carbon skeleton but with different positions of one of the two double bonds — 3,5-dimethyl-2,4-heptadiene and 3-methyl-5-ethyl-3,5-hexadiene) [2].



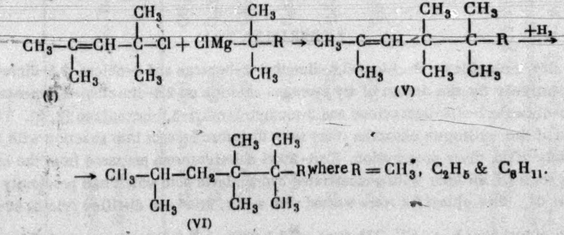
$$\underset{(Ia)}{CH_3-\underset{CH_3}{C}=CH-\overset{CH_3}{\underset{CH_3}{C}}-Br} + RMgBr \rightarrow \underset{(III)}{CH_3-\underset{CH_3}{C}=CH-\overset{CH_3}{\underset{CH_3}{C}}-R}$$

$$\underset{(IIa)}{C_2H_5-\underset{CH_3}{C}=CH-\overset{C_2H_5}{\underset{CH_3}{C}}-Br} + RMgBr \rightarrow \underset{(IV)}{C_2H_5-\underset{CH_3}{C}=CH-\overset{C_2H_5}{\underset{CH_3}{C}}-R}$$

The yields of alkenes were 30%; the structure of some of them was confirmed by ozonization [1-3].

Subsequent investigation of this reaction showed that the yields of alkenes (III) can be raised to 50% by using a tertiary allyl chloride of structure (I) (hydrochloride of 2,4-dimethyl-1,3-pentadiene) in place of the corresponding bromide [3, 4].

In the present work we studied the reaction between tert-allyl chlorides $C_7H_{12}Cl$ and $C_9H_{17}Cl$ with structures (I) and (II) and organomagnesium compounds containing a tert-alkyl group as a method of synthesis of alkenes (V) and (VI) with two adjacent quaternary carbon atoms.



$$\underset{(I)}{CH_3-\underset{CH_3}{C}=CH-\overset{CH_3}{\underset{CH_3}{C}}-Cl} + ClMg-\overset{CH_3}{\underset{CH_3}{C}}-R \rightarrow \underset{(V)}{CH_3-\underset{CH_3}{C}=CH-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-R} \xrightarrow{+H_2}$$

$$\rightarrow \underset{(VI)}{CH_3-\underset{CH_3}{CH}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-R} \text{ where } R = CH_3^*,\ C_2H_5\ \&\ C_6H_{11}.$$

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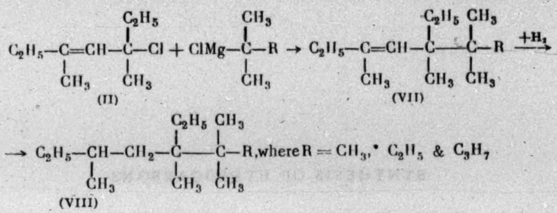
* We previously synthesized [5] the alkenes and alkanes of structures (V), (VII) and (VI), (VIII), in which R = CH_3, from the corresponding tertiary allyl bromides (Ia and IIa).



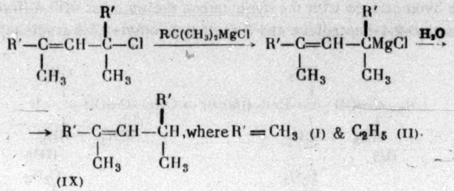
$$C_2H_5{-}C(CH_3){=}CH{-}C(CH_3)(C_2H_5){-}Cl + ClMg{-}C(CH_3)_2{-}R \rightarrow C_2H_5{-}C(CH_3){=}CH{-}C(CH_3)(C_2H_5){-}C(CH_3)_2{-}R \xrightarrow{+H_2}$$

(II) (VII)

$$\rightarrow C_2H_5{-}CH(CH_3){-}CH_2{-}C(C_2H_5)(CH_3){-}C(CH_3)_2{-}R\text{, where } R = CH_3,^{*}\ C_2H_5\ \&\ C_3H_7$$

(VIII)

Referring to the above equations, we see that the method was employed for synthesis of olefinic and paraffinic hydrocarbons of structures (V)-(VIII) containing 11-15 carbon atoms, as well as cyclohexanic hydrocarbons containing 16 carbon atoms with two quaternary carbon atoms in the side chain. The yields of unsaturated hydrocarbons (V) and (VII) were no more than 2-14% (calculated on the tert-alkyl magnesium chlorides whose content in the ethereal solution was determined by titration), due to secondary reactions involving facile cleavage of hydrogen chloride from the tertiary allyl chlorides (I) and (II) with formation of the original alkadienes C_7H_{12} and C_9H_{16} or their dimers, and also due to exchange reaction of these chlorides with the organomagnesium compounds so that after decomposition of the reaction mixture with water the alkenes (IX) C_7H_{14} and C_9H_{18} were formed [2, 5].



$$R'{-}C(CH_3){=}CH{-}C(CH_3)(R'){-}Cl \xrightarrow{RC(CH_3)_2MgCl} R'{-}C(CH_3){=}CH{-}C(CH_3)(R')MgCl \xrightarrow{H_2O}$$

$$\rightarrow R'{-}C(CH_3){=}CH{-}CH(CH_3)(R')\text{, where } R' = CH_3\ (I)\ \&\ C_2H_5\ (II)$$

(IX)

Olefinic hydrocarbons with two adjacent quaternary carbon atoms (V) and (VII) were isolated from the mixture of reaction products by two fractional distillations in a column. The Raman spectra of these hydrocarbons contained double-bond frequencies in the 1658-1668 cm^{-1} region which confirmed their structure as trisubstituted olefins; the spectra of the corresponding alkanes contained strong lines in the 660-678, 930 and 1204-1240 cm^{-1} regions, which are characteristic [6, 7] of complex branching (quaternary carbon atom) in a carbon chain.

Reactions between tertiary allyl chlorides and tert-alkyl magnesium chlorides can consequently serve as a method of synthesis of hydrocarbons with two adjacent quaternary carbon atoms. It should be noted that in the case of all of the alkenes that we synthesized (except the first one) and of the C_{11}-C_{15} alkanes the molecular refractions (MR_D) found were very different (EM_D from -0.36 to -1.00) from those calculated by the usual procedure (from the atomic refractions); at the same time the molar refractions of these hydrocarbons calculated by the additive procedure of V. M. Tatevskii [8], with allowance for the subtypes of chemical bond, are in good agreement with our experimental values (see Tables 1 and 2).

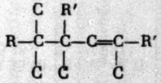
EXPERIMENTAL

The tert-allyl chlorides – 2-chloro-2,4-dimethyl-3-heptene and 3-chloro-3,5-dimethyl-4-heptene – were obtained, respectively by the action of dry hydrogen chloride on 2,4-dimethyl-1,3-pentadiene [3, 4] and on a mixture of 3,5-dimethyl-2,4-heptadiene and 3-methyl-5-ethyl-3,5-hexadiene [2, 5]. The chlorides broke down on distillation of the hydrogen chloride; they were therefore brought into reaction with tert-alkyl magnesium chlorides immediately after their preparation. Tert-alkyl chlorides were prepared from the corresponding tert-alcohols by shaking for half an hour with concentrated hydrochloric acid which had previously been saturated with hydrogen chloride at 0°. The chlorides were washed with water, dried and distilled (yields 80-90%).

Tert-butyl chloride: b. p. 50° (736 mm), $n^{20}D$ 1.3859, d_4^{20} 0.847. Tert-amyl chloride: b. p. 84-85° (744 mm), $n^{20}D$ 1.4047, d_4^{20} 0.8623. 2-Chloro-2-methylpentane: b. p. 105-106° (740 mm), $n^{20}D$ 1.4125, d_4^{20} 0.8605. 2-Chloro-2-cyclohexylpropane: b. p. 78° (12 mm), $n^{20}D$ 1.4708, d_4^{20} 0.9626; MR_D 46.62; calc. 46.43.

TABLE 1

Constants and Yields of C_{11}–C_{16} Hydrocarbons of the Structure



$R{-}C(C)(C){-}C(R')(C){-}C{=}C(C){-}R'$ (V and VII)

General formula	R′	R	Name	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D			Frequency of double bond in Raman spectrum	Yield	
							found	calculated			in g	in % calc. on organo-magnesium compound formed***
								allowing for sub-types of bond [8]	from atomic refractions			
$C_{11}H_{22}$ *	CH_3	CH_3	2,2,3,3,5-Pentamethyl-4-hexene	172° (745)	1.4470	0.7855	52.49	52.33	52.53	1664	52	14
$C_{12}H_{24}$	CH_3	C_2H_5	3,3,4,4,6-Pentamethyl-5-heptene	198.5—199 (750)	1.4589	0.8099	56.79	56.72	57.15	1668	41	11
$C_{13}H_{26}$ **	C_2H_5	CH_3	2,2,3,5-Tetramethyl-3-ethyl-4-heptene	71.5—72.5 (6)	1.4552	0.8076	61.27	61.24	61.76	1660	31	13
$C_{14}H_{28}$	C_2H_5	C_2H_5	3,3,4,6-Tetramethyl-4-ethyl-5-octene	97.5—98 (8)	1.4620	0.8226	65.61	65.63	66.38	1658	41	10.5
$C_{15}H_{30}$	C_2H_5	C_3H_7	4,4,5,7-Tetramethyl-5-ethyl-6-nonene	238—239 (760)	1.4690	0.8345	70.21	70.26	71.00	—	11	2
$C_{16}H_{30}$	CH_3	C_6H_{11}	2,3,3,5-Tetramethyl-2-cyclohexyl-4-hexene	125—127 (4)	1.4916	0.8836	72.98	—	73.42	—	13	10

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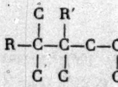
* Literature data: b. p. 170-170.2° (760 mm), $n^{20}D$ 1.4470, d_4^{20} 0.7836, MR_D 52.60 [5]; b. p. 175° (760 mm), $n^{20}D$ 1.4461 (isolated from the mixture of hydrocarbons formed on dimerization of triptene with sulfuric acid [9].

** Literature data [5]: b. p. 210.5-211° (755 mm), $n^{20}D$ 1.4574, d_4^{20} 0.8012, MR_D 61.91.

*** Yields of organomagnesium compounds from tert-C_4H_9Cl, tert-$C_5H_{11}Cl$, tert-$C_6H_{13}Cl$, and 2-chloro-2-cyclohexylpropane were, respectively, 70, 60, 65 and 30%.

TABLE 2

Constants of C_{11}-C_{16} Hydrocarbons of Structure



$$R-\underset{C}{\overset{C}{C}}-\underset{C}{\overset{R'}{C}}-C-\underset{C}{C}-R'$$

(VIandVIII)

General formula	R′	R	Name	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D			Strong frequencies in the Raman spectra characteristic of complex chain branching (cm^{-1})
							found	calculated		
								allowing for sub. types of bond [8]	from atomic refractions	
$C_{11}H_{24}$ *	CH_3	CH_3	2,2,3,3,5-Pentamethylhexane	170° (721)	1.4296	0.7673	52.60	52.55	52.99	678, 926, 1240
$C_{12}H_{26}$	CH_3	C_2H_5	3,3,4,4,6-Pentamethylheptane	189 (730)	1.4402	0.7892	56.92	56.94	57.62	675, 930, 1207
$C_{13}H_{28}$ **	C_2H_5	CH_3	2,2,3,5-Tetramethyl-3-ethylheptane	214—214.2 (725)	1.4470	0.8013	61.45	61.42	62.23	660, 929, 1219
$C_{14}H_{30}$	C_2H_5	C_2H_5	3,3,4,6-Tetramethyl-4-ethyloctane	108.5—109 (9)	1.4540	0.8156	65.85	65.82	66.85	663, 912, 930, 1204, 1219
$C_{15}H_{32}$	C_2H_5	C_3H_7	4,4,5,7-Tetramethyl-5-ethylnonane	122—123(28)	1.4590	0.8197	70.49	70.47	71.47	—
$C_{16}H_{32}$	CH_3	C_6H_{11}	2,3,3,5-Tetramethyl-2-cyclohexylhexane	135—136 (5)	1.4679	0.8464	73.67	—	73.88	753, 930, 1196

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* Literature data [5]: b. p. 172.8-173.5° (760 mm), $n^{20}D$ 1.4302, d_4^{20} 0.7673, MR_D 52.88.

** Literature data [5]: b. p. 214-215° (750 mm), $n^{20}D$ 1.4442, d_4^{20} 0.7934, MR_D 61.80.

TABLE 3

Analytical Results

General formula		$C_{12}H_{24}$	$C_{12}H_{26}$	$C_{14}H_{28}$	$C_{14}H_{30}$	$C_{15}H_{30}$	$C_{15}H_{32}$	$C_{16}H_{30}$	$C_{16}H_{32}$
C	Found %	85.64, 85.81	84.69, 84.86	85.68, 85.84	84.57, 84.72	85.62, 85.77	84.86, 84.69	86.45, 86.32	85.64, 85.80
	Calculated %	85.63	84.62	85.62	84.76	85.63	84.76	86.41	85.63
H	Found %	14.32, 14.36	15.36, 15.10	14.34, 14.37	15.37, 15.18	14.36, 14.42	15.10, 14.98	13.64, 13.36	14.31, 14.39
	Calculated %	14.37	15.38	14.37	15.24	14.37	15.18	13.59	14.37

Reaction of tert-allyl chlorides with tert-alkyl magnesium chlorides. Into an ethereal solution of the organomagnesium compound prepared by slow addition of 2.2 moles tert-alkyl chloride in 800 ml of absolute ether to 2 atoms magnesium (activated with a few drops of methyl iodide) in 350 ml ether, was gradually stirred (cooling to −40°) a 1 : 1 ethereal solution of freshly distilled tert-allyl chloride – 2-chloro-2,4-dimethyl-3-heptene or 3-chloro-3,5-dimethyl-4-heptene – in quantity equimolar with the organomagnesium compound formed (the content of the latter in the ethereal solution was determined in a separate sample by titration – see Table 1). The reaction mixture was stirred for 2 hrs with the same degree of cooling, then for 2 hrs at room temperature, and for several hours with heating. After the reaction mixture had been decomposed (by pouring onto ice containing 10% hydrochloric acid or ammonium chloride), the ethereal extracts were worked up in the usual manner, the ether and the low-boiling fractions (up to 100°) were distilled off, and the residue was boiled with sodium (until the reaction for halogen was negative). The product was distilled off from polymers in vacuo and finally distilled over sodium in a column. Each experiment was carried out twice. Constants and yields of olefinic hydrocarbons with two adjacent quaternary carbon atoms (V and VII), isolated after two distillations in a column,* are presented in Table 1; the analytical results appear in Table 3.

The olefinic hydrocarbons were hydrogenated over nickel on alumina at 170-180°. The catalyzates (which did not decolorize bromine water) were washed with 80% sulfuric acid, with water, and with sodium carbonate until neutral, and distilled over sodium in a column. The constants of the resulting paraffinic hydrocarbons with two adjacent quaternary carbon atoms (VI and VIII) are presented in Table 2, while analytical results appear in Table 3.

SUMMARY

1. Reaction of tert-allyl chlorides with tert-alkyl magnesium chlorides was used as a method of synthesis of olefinic hydrocarbons containing two adjacent quaternary carbon atoms.

2. C_{11}-C_{16} hydrocarbons of the structure in question were synthesized by this method from 2-chloro-2,4-dimethyl-3-pentene (hydrochloride of 2,4-dimethyl-1,3-pentadiene) and 3-chloro-3,5-dimethyl-4-heptene (obtained by hydrochlorination of a mixture of isomeric dienes with the same carbon skeleton but with different positions of one double bond – 3,5-dimethyl-2,4-heptadiene and 3-methyl-5-ethyl-3,5-hexadiene): 2,2,3,3,5-pentamethyl-4-hexene; 2,2,3,5-tetramethyl-3-ethyl-4-heptene; 3,3,4,4,6-pentamethyl-5-heptene; 3,3,4,6-tetramethyl-4-ethyl-5-octene; 4,4,5,7-tetramethyl-5-ethyl-6-nonene; also 2,3,3,5-tetramethyl-2-cyclohexyl-4-hexene. The last four compounds are here described for the first time.

3. Hydrogenation of these olefinic hydrocarbons led to the corresponding paraffinic hydrocarbons with two adjacent quaternary carbon atoms: 2,2,3,3,5-pentamethylhexane; 2,2,3,5-tetramethyl-3-ethylheptane; 3,3,4,4,6-pentamethylheptane; 3,3,4,6-tetramethyl-4-ethyloctane; 4,4,5,7-tetramethyl-5-ethylnonane; also 2,3,3,5-tetramethyl-2-cyclohexylhexane. The last four compounds have not previously been described.

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* In all of the reactions carried out with 2-chloro-2,4-dimethyl-3-pentene (I), distillation gave a fraction consisting of the dimer of 2,4-dimethyl-1,3-pentadiene (b. p. 218-219° at 750 mm; 90° at 10 mm, $n^{20}D$ 1.4800) [1]; the reactions with 3-chloro-3,5-dimethyl-4-heptene (II) gave a fraction whose constants identified it as 3,5-dimethyl-3-heptene (IX, R' = C_2H_5; b. p. 130.5-131° at 750 mm, $n^{20}D$ 14220) [2].

** Original Russian pagination. See C. B. translation.

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Moscow State University

REACTION OF TERT-BUTYLBENZENE β-(MAGNESIUM CHLORIDE) WITH CARBONYL COMPOUNDS

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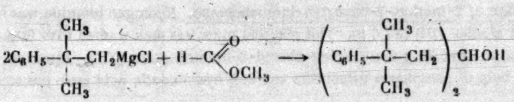
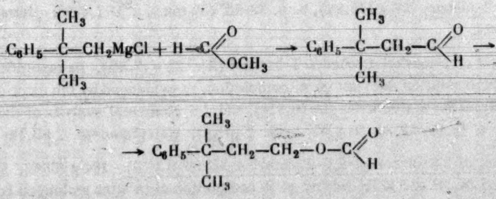
1-Chloro-2-methyl-2-phenylpropane ($C_6H_5-C(CH_3)_2-CH_2Cl$) is easily synthesized by chloroalkylation of benzene with methallyl chloride [1]. No studies have previously been made, however, of the possibilities of utilization of this halide – a structural analog of neopentyl chloride – in organomagnesium synthesis. The present investigation was undertaken with the aim of finding reliable methods of synthesis of alkylbenzenes containing a long branched chain with a quaternary carbon at the ring. As we know, such hydrocarbons were until recently obtained mainly by alkylation of benzene with tertiary alcohols in presence of $AlCl_3$. This method did not always ensure preparation of the pure forms [2]. Condensation of the Grignard reagent from the above halide with aldehydes gives secondary alcohols in high yield (53.5-72.5%). The properties of these alcohols are presented in the table. The yields of tertiary alcohols obtained by reaction of tert. butylbenzene β-(magnesium chloride) with ketones (acetone and methyl ethyl ketone) were very much lower (22 and 37%). This is evidently due to the circumstance that part of the ketone is reduced to secondary alcohol. These ketones are similarly reduced under the action of isobutyl magnesium chloride, as previously established [3].

In the case of methyl formate the main product was a secondary alcohol – 2,6-dimethyl-2,6-diphenyl-4-heptanol – i. e., a compound formed according to the normal mechanism



$$2C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-CH_2MgCl + H-C\begin{matrix}{}^{\nearrow O}\\{}_{\searrow OCH_3}\end{matrix} \longrightarrow \left(C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-CH_2\right)_2CHOH$$

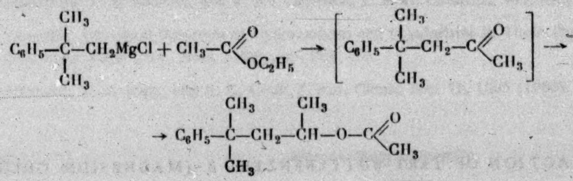
This alcohol or its formic ester was obtained in yields dependent on the conditions of synthesis and ranging between 45 and 68%. Reduction reactions also occur here, as evidenced by the formation of the formic acid ester and a primary alcohol – 3-methyl-3-phenyl-1-butanol (resulting from reduction of the aldehyde).



$$C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-CH_2MgCl + H-C\begin{matrix}{}^{\nearrow O}\\{}_{\searrow OCH_3}\end{matrix} \longrightarrow C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-C\begin{matrix}{}^{\nearrow O}\\{}_{\searrow H}\end{matrix} \longrightarrow$$

$$\longrightarrow C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_2-O-C\begin{matrix}{}^{\nearrow O}\\{}_{\searrow H}\end{matrix}$$

Formic esters of alcohols are products of their transesterification with methyl formate. The reaction of tert-butylbenzene β-(magnesium chloride) with ethyl acetate only went to the stage of formation of ketone (but not of tertiary alcohol), the ketone being reduced to secondary alcohol which was esterified by the ethyl acetate.



$$C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-CH_2MgCl + CH_3-C\begin{smallmatrix}{=}O\\ OC_2H_5\end{smallmatrix} \rightarrow \left[C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-C\begin{smallmatrix}{=}O\\ CH_3\end{smallmatrix}\right] \rightarrow$$

$$\rightarrow C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{CH}-O-C\begin{smallmatrix}{=}O\\ CH_3\end{smallmatrix}$$

The ketone was evidently reduced by addition of 2MgCl at the carbonyl group, as evidenced by secondary formation of the hydrocarbon 2,5-dimethyl-2,5-diphenylhexane $C_6H_5C(CH_3)_2CH_2CH_2C(CH_3)_2C_6H_6$. The reaction with trimethylacetyl chloride evidently went in similar fashion. Here, however, the ester of the secondary alcohol was accompanied by the free alcohol 2,5,5-trimethyl-2-phenyl-4-hexanol (VI). This alcohol could be prepared in the pure form by reaction of tert-butyl magnesium chloride with β-phenylisovaleryl chloride.

EXPERIMENTAL

Reaction of tert-butylbenzene β-(magnesium chloride) with aldehydes and ketones. The reaction was performed under standard conditions with the same ratios of components in all of the experiments. An excess of carbonyl compound was taken. We give details of a typical experiment. In the course of 4 hrs 200 g β-chloro-tert-butylbenzene was added, after reaction had commenced, to 48.6 g magnesium in 500 ml ether. After completion of the addition, the mass was stirred for 1 hr. Addition was then made of 130 g isovaleraldehyde and stirring was continued for another 12 hrs. After the reaction mass had been decomposed with water and weak hydrochloric acid, 168 g (61%) 2,7-dimethyl-2-phenyl-4-heptanol was isolated from the ethereal solution. In other experiments tert-butylbenzene β-(magnesium chloride) was reacted with acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, acetone and methyl ethyl ketone. The properties of the synthesized alcohols – 2-methyl-2-phenyl-4-pentanol (I), 2-methyl-2-phenyl-4-hexanol (II), 2-methyl-2-phenyl-4-heptanol (III), 2,5-dimethyl-2-phenyl-4-hexanol (IV), 2,7-dimethyl-2-phenyl-4-heptanol (V), 2,5-dimethyl-2-phenyl-4-pentanol (VII) and 2,5-dimethyl-2-phenyl-4-hexanol (VIII) – and their yields are presented in the table.

Preparation of 2-methyl-2-phenyl-4-bromoheptane. Hydrogen bromide was bubbled at 100° for 16 hrs through a layer of alcohol (III) (87.5 g). The reaction mass was then washed with 90% sulfuric acid and water, dried, and distilled to give 70 g 2-methyl-2-phenyl-4-bromoheptane (XV). Attempts to replace the hydroxyl by bromine with the help of phosphorus tribromide and 40% hydrobromic acid were unsuccessful.

Reaction of tert-butylbenzene β-(magnesium chloride) with esters. 1) Reaction with methyl formate. A. 180 g methyl formate diluted with twice as much ether was added with continuous stirring to tert-butylbenzene β-(magnesium chloride), prepared from 253 g β-chloro-tert-butylbenzene and 60 g Mg, at 5° in the course of 2 hrs. Considerable heat was developed during the reaction. The following substances were separated by fractional distillation:

Tert-butylbenzene: 30 g (14.8%), b. p. 82-85° (50 mm), $n^{20}D$ 1.4930; literature data [1]: b. p. 84.2° (50 mm), $n^{20}D$ 1.4924.

Formic ester of 2-methyl-2-phenyl-1-butanol (X): 21 g (7.3%). Its saponification with 5% alcoholic and 10% aqueous NaOH solution does not go to completion, as evidenced by the ester number (found 265.95; calculated 291.8), analyses for active hydrogen (0.818), and the elemental analysis of the alcohol obtained by saponification. Found %: C 79.15, 79.36; H 9.47, 9.43. $C_{11}H_{16}O$. Calculated %: C 80.44; H 9.82.

Formic ester of 2,6-dimethyl-2,6-diphenyl-4-heptanol (XII): 164 g (68%). Its saponification with 10% alcoholic solutions of NaOH and KOH did not go to completion even after prolonged boiling, as indicated by its ester number (found 163.3, calculated 172.9), and by the properties of the substance (b. p. 174°, at 1 mm, $n^{20}D$ 1.5420, d_4^{20} 1.0100) obtained by saponification, which did not correspond either to those of the original ester or of alcohol (IX) (see table). The ester is not saponified at all by 10% aqueous NaOH.

B. Instead of the ethereal solution of methyl formate being added to the Grignard reagent, the reverse procedure was followed. The same quantities of starting components were taken and the Grignard reagent was

Substance No.	Structure and name of compound	Yield (%)	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D			Analysis				
						calc. from refractions		found	found (%)		empirical formula	calculated (%)	
						of atoms	of bonds		C	H		C	H
(I)	$C_6H_5C(CH_3)_2CH_2CHOHCH_3$ 2-Methyl-2-phenyl-4-pentanol	72.5	148—149° (13)	1.5130	0.9697	55.54	55.87	55.25	—	—	—	—	—
(II)	$C_6H_5C(CH_3)_2CH_2CHOHC_2H_5$ 2-Methyl-2-phenyl-4-hexanol	72.7	112—113 (4)	1.5100	0.9592	60.15	60.51	59.95	81.07, 81.08	10.56, 10.63	$C_{13}H_{20}O$	81.19	10.48
(III)	$C_6H_5C(CH_3)_2CH_2CHOHC_3H_7$ 2-Methyl-2-phenyl-4-heptanol	53.5	128 (2)	1.5030	0.9470	64.78	65.16	64.51	80.90, 80.97	10.23, 10.07	$C_{14}H_{22}O$	81.48	10.76
(IV)	$C_6H_5C(CH_3)_2CH_2CHOHCH(CH_3)_2$ 2,5-Dimethyl-2-phenyl-4-hexanol	56.0	95.5 (2.5)	1.5072	0.9516	64.78	65.16	64.65	81.00, 80.92	10.67, 10.68	$C_{14}H_{22}O$	81.48	10.76
(V)	$C_6H_5C(CH_3)_2CH_2CHOHCH_2CH(CH_3)_2$ 2,7-Dimethyl-2-phenyl-4-heptanol	61.0	117 (2)	1.5021	0.9366	69.39	69.83	69.43	82.01, 81.87	10.99, 11.01	$C_{15}H_{24}O$	81.75	10.49
(VI)	$C_6H_5C(CH_3)_2CH_2CHOHC(CH_3)_3$ 2,5,5-Trimethyl-2-phenyl-4-hexanol	58.5	113—114 (3)*	—	—	—	—	—	81.44, 81.43	10.86, 10.80	$C_{15}H_{24}O$	81.75	10.49
(VII)	$C_6H_5C(CH_3)_2CH_2C(CH_3)_2OH$ 2,5-Dimethyl-2-phenyl-4-pentanol	22.6	108.5—109 (4)	1.5130	0.9629	60.15	60.51	60.02	80.42, 80.38	10.60, 10.46	$C_{13}H_{20}O$	81.19	10.48
(VIII)	$C_6H_5C(CH_3)_2CH_2C(CH_3)(OH)C_2H_5$ 2,5-Dimethyl-2-phenyl-4-hexanol	37.0	101—101.5 (1.5)	1.5094	0.9565	64.78	65.16	64.44	—	—	—	—	—
(IX)	$C_6H_5C(CH_3)_2CH_2CHOHCH_2C(CH_3)_2C_6H_5$ 2,6-Dimethyl-2,6-diphenyl-4-heptanol	55.0	167—168 (1)	1.5428	1.008	93.50	94.21	93.41	84.46, 84.71	9.51, 9.50	$C_{21}H_{28}O$	85.08	9.52
(X)	$C_6H_5C(CH_3)_2CH_2CH_2OOCH$ Formic ester of 2-methyl-2-phenyl-1-butanol	7.3	81 (2)	1.5070	1.0204	55.67	56.05	56.07	74.85, 74.75	8.24, 8.21	$C_{12}H_{16}O_2$	74.96	8.38
(XI)	$C_6H_5C(CH_3)_2CH_2CH(CH_3)OCOCH_3$ Acetic ester of 2-methyl-2-phenyl-4-pentanol	17.6	101—102 (3)	1.4980	0.9966	64.80	65.39	64.78	76.53, 76.47	8.71, 8.79	$C_{14}H_{20}O_2$	76.32	9.15
(XII)	$C_6H_5C(CH_3)_2CH_2CH(OOCH)CH_2C(CH_3)_2C_6H_5$ Formic ester of 2,6-dimethyl-2,6-diphenyl-4-heptanol	68.0	174.5 (2)	1.5350	1.0279	98.25	99·08	98.27	81.68, 81.69	8.73, 8.72	$C_{22}H_{28}O_2$	81.44	8.7
(XIII)	$C_6H_5C(CH_3)_2CH_2CH{=}CHC(CH_3)_2C_6H_5$ 2,6-Dimethyl-2,6-diphenyl-4-heptene	94.5	140—141° (2)	1.5445	0.9578	91.51	92.21	91.65	90.35, 90.63	9.55, 9.55	$C_{21}H_{26}$	90.58	9.42
(XIV)	$C_6H_5C(CH_3)_2CH_2COCl$ β-Phenylisovaleryl chloride	94.0	97 (2)	1.5220	1.1023	54.64	54.49	54.42	—	—	—	—	—
(XV)	$C_6H_5C(CH_3)_2CH_2CHBrC_3H_7$ 2-Methyl-2-phenyl-4-bromoheptane	61.0	121—125 (2)	1.5170	1.1455	71.02	71.35	70.99	62.60, 62.68	8.09, 8.01	$C_{14}H_{21}Br$	62.44	7.86

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* M. p. 45.5°.

introduced in the course of an hour, after which the reaction mixture was stirred for another 6 hrs at the boiling point of ether. The reaction gave 21% tert-butylbenzene, 21% of the formic ester of 2-methyl-2-phenyl-1-butanol (X) and 49.2% of the formic ester of 2,6-dimethyl-2,6-diphenyl-4-heptanol (XII).

C. 38 g of methyl formate, diluted with double the quantity of ether, was run into the tert-butylbenzene β-(magnesium chloride) prepared from 316 g β-chloro-tert-butylbenzene and 60 g Mg at the boiling point of ether. The reaction mixture was then stirred for another 1 hr. Fractional distillation gave the following substances:

Tert-butylbenzene: 52.5 g (23.3%), b. p. 85-87° (53 mm), $n^{20}D$ 1.4924; and 2,6-dimethyl-2,6-diphenyl-4-heptanol (IX): 103 g (55%).

Dehydration of 2,6-dimethyl-2,6-diphenyl-4-heptanol. 25 g of the alcohol was heated for an hour at 100° with 8 g oxalic acid. Fractional distillation gave 22 g (94%) of 2,6-dimethyl-2,6-diphenyl-4-heptene (XIII).

2) Reaction with ethyl acetate was performed under the same conditions as with methyl formate, using 260 g β-chloro-tert-butylbenzene, 50 g Mg and 264 g ethyl acetate. The Grignard reagent was run into the ethereal solution of ethyl acetate. Considerable heat was developed. Fractional distillation of the reaction products gave the following:

Tert-butylbenzene: 114 g (59%), b. p. 89-90° (60 mm), $n^{20}D$ 1.4910; acetic ester of 2-methyl-2-phenyl-4-pentanol (XI): 29 g (17.6%); 2,5-dimethyl-2,5-diphenylhexane: 37 g (20.5%), b. p. 157-158° (3 mm), m. p. 59.5-60°. Literature [4]: m. p. 60-61°. Found %: C 89.95, 89.97; H 10.01, 9.98. $C_{20}H_{26}$. Calculated %: C 90.01; H 9.87.

Synthesis of 2,5,5-trimethyl-2-phenyl-4-hexanol (VI). β-Phenylisovaleric acid with m. p. 59° was obtained in 81% yield by passage of gaseous CO_2 through tert-butylbenzene β-(magnesium chloride). The literature [1] reports m. p. 58-59°. A solution of 150 g of the acid in 250 ml chloroform was added with vigorous stirring to 430 g PCl_5. Considerable heat was generated. After the acid had been added, the reaction mixture was stirred for another 12 hrs and with heating to 50° during the final 6 hrs. 160 g β-phenylisovaleryl chloride (XIV) was obtained.

Tert-butyl magnesium chloride prepared from 139 g tert-butyl chloride and 48 g Mg was added at 3° in the course of an hour to an ethereal solution of 142 g acid chloride (XIV). After the addition was completed, the mixture was stirred for another 2 hrs. The reaction gave 89 g of alcohol (VI). Found 0.975 OH group per molecule of alcohol.

SUMMARY

1. The Grignard reagent from 1-chloro-2-methyl-2-phenylpropane — tert-butylbenzene β-(magnesium chloride) — reacts in the normal manner with aldehydes to form secondary alcohols in a yield of 53-73%.

2. The same Grignard reagent reacts with ketones to form tertiary alcohols in considerably lower yields (22-37%), since the ketones are partly reduced by it to secondary alcohols.

3. Reaction of tert-butylbenzene β-(magnesium chloride) with methyl formate goes mainly according to the normal mechanism with formation of secondary alcohol or its formic ester. With ethyl acetate the reaction only goes to the stage of formation of ketone which is then reduced to secondary alcohol and is esterified.

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INVESTIGATIONS ON CONJUGATED SYSTEMS

XCII. SEQUENCE OF ADDITION OF IODINE TO VINYLACETYLENIC HYDROCARBONS*

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In preceding papers it was shown that the sequence of addition of bromine to vinylacetylenic hydrocarbons depends on their structure. Whereas unconjugated vinylacetylenes and vinylalkylacetylenes add on bromine at the double bond, unsubstituted vinylacetylene and alkenylacetylenes add bromine predominantly in the 1,4-position with formation of allenic halo derivatives. This behavior was attributed to changes in distribution of the electronic density in the conjugated system under the influence of radicals [1-5].

It was interesting to compare the sequence of addition of different halogens to vinylacetylenic hydrocarbons. We know that in the case, for example, of butadiene, iodine adds on only in the 1,4-position, whereas bromine, and more so chlorine, give considerable quantities of 1,2-products [6]. With this objective we also investigated the sequence of addition of iodine to vinyl-, vinylmethyl-, vinylethyl-, propenyl- and allylmethylacetylenes. The literature contains data only for the reaction of vinylacetylene with iodine, and the structure of the adduct was not elucidated [7].

All of the reactions of this class that we investigated were considerably speeded up by light, so that a radical mechanism is definitely involved. Iodine added very slowly in the dark.

The resulting diiodides were heavy oils which were colored by iodine. Their structure was determined through the infrared spectra.**

The spectrum of diiodovinylacetylene contains strong frequencies of a conjugated system of double bonds (1616 cm^{-1}) and of the vinyl grouping (926, 966 and 6060 cm^{-1}). There was no trace of the frequencies of about 2100 and 3300 cm^{-1} which characterize a terminal acetylenic grouping. Nor did the spectrum contain frequencies characteristic of the allenic system (1960 cm^{-1}). The neighboring weak frequency of 1920 cm^{-1} is observed in the spectra of many dienic compounds. Strong absorption at 760 cm^{-1} bears witness to the cis-configuration of at least the greater part of the product.

It has thus been established that iodine adds onto vinylacetylene at the acetylenic bond.

The same conclusions are reached when we consider the spectra of the diiodo derivatives of vinylmethyl and vinylethylacetylenes. Here the conjugated system of double bonds is associated with the extremely intense 1603 cm^{-1} frequency, and the vinyl group has strong frequencies at 917 and 965 cm^{-1}, as well as a characteristic overtone at 6060 cm^{-1}. Very weak absorption is observed in the normal region of absorption of disubstituted acetylenes, and this is probably an overtone. The 1960 cm^{-1} frequency is absent from the spectrum. Consequently, the sequence of addition of iodine to vinylalkylacetylenes does not differ from that in the case of unsubstituted vinylacetylene.

Apart from the strong bands due to the $-CH{=}CH-$ grouping (947 and 1640 cm^{-1}), the spectrum of diiodopropenylacetylene also contains a weak band at 1971 cm^{-1} which is suggestive of the presence of a very small

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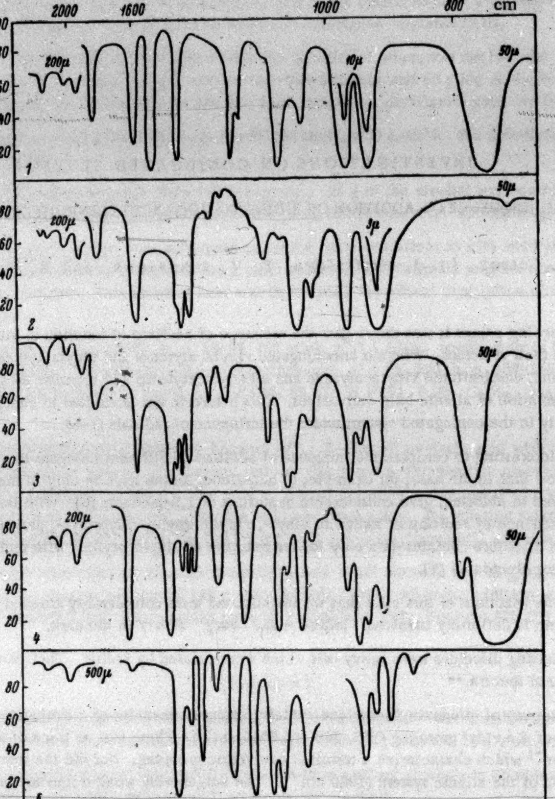
* Enynic compounds. XXI.

** Investigations were carried out both on the distilled substances and on products obtained by removal of the solvent and starting hydrocarbon from the reaction mixture in vacuo at a temperature not exceeding 20°. The spectra of the latter contained many weak frequencies in the region above 2000 cm^{-1}. No differences in position and intensity of the principal frequencies were observed. Distillation is therefore not accompanied by isomerization.



Infrared transmission spectra of diiodo compounds. 1) Vinylacetylene; 2) vinylmethylacetylene; 3) vinylethylacetylene; 4) propenylacetylene (2nd fraction); 4) allylmethylacetylene (crystalline product with m. p. 65°); 6) allylmethylacetylene (liquid).

quantity of 1,4-adduct in the diiodo derivative. The 2102 cm^{-1} frequency can be assigned to the valence vibration of the terminal acetylenic bond, but the usually very much more intense frequency of the valence vibrations of the acetylenic hydrogen is entirely absent. The frequency at about 2100 cm^{-1} is therefore an overtone.

It has thus been established that conjugated vinylacetylenes add on iodine at the acetylenic bond regardless of the structure.

Iodine adds on to allylmethylacetylene with great facility at both of the multiple bonds: the main product of the reaction when equimolar quantities of iodine and hydrocarbon are mixed is the tetraiodo compound. No tetraiodo compound was detected when conjugated vinylacetylenes were reacted, evidently due to steric hindrance. Two diiodo compounds were formed in addition to the tetraiodo compound: a liquid and a crystalline substance. The spectrum of the liquid contains a strong double-bond band (1640 cm^{-1}); in this region the spectrum of the solid substance exhibits only weak absorption.

The observed differences in the sequence of addition of bromine and iodine to vinylacetylenic hydrocarbons are evidently associated with differences in reaction mechanisms: bromine adds on by ionic or molecular mechanism and iodine by a well-marked radical mechanism.

Selective addition of atomic iodine at the acetylenic bond is determined in our opinion by the greater stability of the transition complex formed in this case. Interaction of a free electron of the iodine atom with the π-electrons of the triple bond can result in conjugation of this electron with the entire enynic system. Such a conjugation does not occur, however, when the site of addition is the double bond.

Hydrogenation of vinylacetylenic hydrocarbons is most probably also accompanied by radical addition of hydrogen atoms, and as in the case of iodine addition to the reaction takes place at the actylenic bond [8].

EXPERIMENTAL

Addition of Iodine to Vinylacetylenic Hydrocarbons

Vinylacetylene. A solution of 20 ml of vinylacetylene in 30 ml ethyl chloride and 50.8 g iodine were exposed for several hours in diffused light in a closed vessel which was shaken periodically. After decolorization had occurred, the ethyl chloride was evaporated off and the residue was distilled in vacuo. The following fractions were obtained: 1st, to 84°, 3.7 g; 2nd, 84-85°, 49 g; residue 3.0 g.

The following constants were found for 1,2-diiodo-1,3-butadiene[•]:

B. p. 84-84.5° (5 mm), d_4^{20} 2.5652, $n^{20.1}\alpha$ 1.7082, $n^{21.7}D$ 1.7165. MR_α 46.51; calc. 43.90. Found %: I 82.47, 82.55. $C_4H_4I_2$. Calculated %: I 82.98.

Infrared spectrum[••] (cm^{-1}): 763 very strong, 926 very strong, 966 very strong, 1056 medium, 1103 very strong, 1173 very weak, 1202 medium, 1232 strong, 1404 very strong, 1524 very strong, 1616 strong, 1840 medium, 1920 weak, 2035 weak, 2204 very weak, 2849 weak, 2921 strong, 2967 very strong, 3001 medium, 3050 strong, 3082 very strong.

Vinylmethylacetylene. Under the same conditions, 25 g iodine and 8 g vinylmethylacetylene gave a product which on distillation in vacuo (5 mm) yielded the following fractions: 1st, to 94°, 2.5 g; 2nd, 94-95°, 24.5 g; residue 2.7 g.

The following constants were found for 2,3-diiodo-1,3-pentadiene:

B. p. 94-94.5° (5 mm), d_4^{20} 2.3781, $n^{20}\alpha$ 1.6886, MR_α 51.34; calc. 48.50. Found %: I 79.44. $C_5H_6I_2$. Calculated %: I 79.34.

Infrared spectrum (cm^{-1}): 760 very weak, 917 very strong, 965 very strong, 1030 strong, 1064 very strong, 1102 very weak, 1144 medium, 1270 weak, 1298 weak, 1373 very strong, 1401 very strong, 1603 very strong, 1830 medium, 1920 weak, 2027 weak, 2092 very weak, 2162 very weak, 2239 weak, 2713 medium, 2790 medium, 2824 strong, 2908 very strong, 2954 strong, 2977 strong, 3003 strong, 3105 very strong.

The reaction went to the extent of 10% when a chloroform solution of the hydrocarbon and iodine with a concentration of 0.1 mole/liter stood in the dark for 3 days. In diffused light the reaction was completed in 3 hrs.

[•] Diiodovinylacetylene is reported [7] to have b. p. 91.5-92° (3 mm).

[••] The infrared transmission spectra were plotted with the IKS-12 spectrograph with an LiF prism in the region up to 5.5 μ, and subsequently with a NaCl prism.

Vinylethylacetylene. The product obtained from 50.8 g iodine and 17 g hydrocarbon in 30 ml ethyl chloride gave the following fractions on distillation in vacuo (5 mm): 1st, to 101°, 5.0 g; 2nd, 101-103°, 37.7 g; residue 5.2 g.

The following constants were found for 2,3-diiodo-1,3-hexadiene:

B. p. 101-103° (5 mm), d_4^{20} 2.2175, $n^{20.1}\alpha$ 1.6639, MR_α 55.85; calc. 53.09. Found %: I 75.88, 76.66. $C_6H_8I_2$. Calculated %: I 76.01.

Infrared spectrum (cm^{-1}): 787 very strong, 916 very strong, 947 weak, 964 very strong, 1035 weak, 1072 very strong, 1088 very strong, 1146 strong, 1255 medium, 1308 medium, 1378 strong, 1402 very strong, 1421 strong, 1453 very strong, 1606 very strong, 1830 medium, 1920 weak, 2045 very weak, 2220 weak, 2814 weak, 2848 medium, 2865 very strong, 2925 very strong, 2954 very strong, 3000 medium, 3095 strong.

Propenylacetylene. 12.7 g iodine and 3.8 g hydrocarbon gave 15 g of a substance which was resolved into the following fractions on distillation: 1st, to 93°, 1.0 g; 2nd, 93.5-94.5°, 3.5 g; 3rd, 95-97°, 4.5 g; 4th, 97-102°, 3.1 g; residue 1.2 g.

The following constants were found for the 2nd fraction:

d_4^{20} 2.3410, $n^{20.1}\alpha$ 1.6827, $n^{20}D$ 1.6860, MR_α 51.81; calc. 48.50. Found %: I 78.46, 78.62. $C_5H_6I_2$. Calculated %: I 79.34.

Infrared spectrum (cm^{-1}): 720 very strong, 801 weak, 910 strong, 931 strong, 947 very strong, 970 strong, 1035 weak, 1060 very strong, 1090 medium, 1110 very strong, 1205 very strong, 1280 strong, 1360 medium, 1377 medium, 1402 medium, 1453 very strong, 1640 very strong, 1971 medium, 2102 weak, 2841 strong, 2860 medium, 2901 very strong, 2930 very strong, 2964 strong, 3012 strong, 3060 very strong, 3080 very strong.

The compound did not lose iodine when stood with 5% alcoholic KOH for 2 hrs.

Found for the 3rd fraction:

d_4^{20} 2.3427, $n^{20}\alpha$ 1.6836, MR_α 51.73; calc. 48.50.

Found for the 4th fraction: d_4^{20} 2.3470.

Found %: I 79.66. $C_5H_6I_2$. Calculated %: I 79.34.

The compound loses about 25% iodine when stood with 5% KOH solution.

The intensity and position of the frequencies associated with the multiple bonds do not differ from those given for the 2nd fraction.

Allylmethylacetylene. Fairly rapid decolorization occurred when a solution of 8 g hydrocarbon in 30 ml ethyl chloride was shaken with 25 g iodine, and a crystalline precipitate was formed (16 g, 55% of the total reaction products). The latter was separated and recrystallized from carbon tetrachloride. M. p. 103-105°. Sparingly soluble in the usual organic solvents.

Found %: I 87.25, 85.76. $C_6H_8I_4$. Calculated %: I 86.37.

5 g of a crystalline substance came down from the liquid after evaporation.

M. p. 65° (from CCl_4). Very much more soluble than the tetraiodo compound.

Found %: I 78.07, 78.10. $C_6H_8I_2$. Calculated %: I 76.01.

Infrared spectrum (cm^{-1}) in CCl_4: 886 weak, 902 strong, 925 medium, 943 strong, 1054 strong, 1107 very strong, 1135 very strong, 1184 very strong, 1230 very strong, 1290 medium, 1355 strong, 1382 medium, 1427 very strong, 1644 very weak (?), 2052 very weak, 2240 weak, 2734 medium, 2815 medium, 2854 strong, 2888 strong, 2917 very strong, 2964 strong, 3028 medium, 3092 weak.

The oil left after the crystals had been separated was distilled in vacuo (4 mm) to give the following fractions: 1st, to 97°, 2 g; 2nd, 97-98°, 6.1 g; residue, 3.5 g. All of these fractions partly crystallized on standing. The crystals deposited from the 2nd fraction were collected (1.3 g, m. p. 65°), and the liquid was examined. The following data were obtained:

d_4^{20} 2.1810, $n^{20.2}_{\alpha}$ 1.6395, MR_{α} 55.13; calc. 53.09. Found %: I 75.25, 75.15. $C_6H_8I_2$. Calculated %: I 76.01.

Infrared spectrum (cm^{-1}): 778 weak, 811 weak, 871 weak, 888 medium, 920 very strong, 964 very strong, 976 very strong, 988 very strong, 1055 strong, 1103 strong, 1120 very weak, 1180 medium, 1202 strong, 1284 medium, 1292 weak, 1350 very weak, 1375 strong, 1427 very strong 1640 very strong.

The crystalline diiodo compound constituted 28% and the liquid 17% of the total product.

SUMMARY

1. The sequence of addition of iodine to five vinylacetylenic hydrocarbons was investigated: vinyl-, vinylmethyl-, vinylethyl-, propenyl- and allylmethylacetylenes.

2. It was shown that, except with the last compound, iodine adds on at the acetylenic bond. It adds on to allylmethylacetylene at both of the multiple bonds with considerable formation of the tetraiodo compound.

3. The reaction is accelerated by light, and therefore a chain radical mechanism is involved.

4. It is suggested that the difference in the sequence of addition of iodine and bromine to vinylacetylenic hydrocarbons is associated with different mechanisms of addition (an ionic mechanism was previously proposed for addition of bromine).

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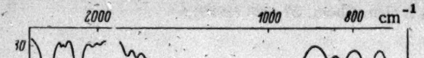
INVESTIGATIONS ON CONJUGATED SYSTEMS

XCIII. THE SEQUENCE OF ADDITION OF ALKYL HYPOBROMITES TO VINYLALKYLACETYLENES*

A. A. Petrov, Iu. I. Porfir'eva, and G. I. Semenov

In preceding communications we showed that vinylalkylacetylenes add on hydrogen [1] and iodine [2] at the triple bond, bromine [3] and alkyl hypobromites [4] at the double bond, and hydrogen halides [5] predominantly in the 1,4-position. These differences in the sequence of addition of bromine and iodine were thought to be due to differences in reaction mechanism (ionic in one case and radical in the other). Concerning the differences in order of addition of bromine and hydrogen bromide, these were correlated with the inability of the triple bond to give a transition π-complex with bromine, whereas hydrogen halides form such complexes with facility.

The structure of the products of addition of all of these substances to vinylacetylenes was determined by chemical methods and with the help of their infrared spectra (except in the case of products of addition of alkyl hypobromites, for which the second technique was not used). Since infrared spectra are the most sensitive and reliable means of determination of the structure of isomeric products of addition of various substances to vinylacetylenic hydrocarbons [6], we repeated the experiments on addition of alkyl hypobromites to vinylalkylacetylenes and investigated the spectra of the resulting bromoethers and the products of their dehydrobromination.



Infrared transmission spectra. 1) Bromoether from vinylmethylacetylene, 2) bromoether from vinylethylacetylene (obtained by the action of bromine on an alcoholic solution of hydrocarbon), 3) bromoether from vinylpropylacetylene, 4) bromoether from vinylbutylacetylene, 5) enol ether obtained from vinylmethylacetylene.

The infrared spectra of all of the bromoethers (see diagram) contained a strong triple bond band, usually consisting of several frequencies in close proximity with a maximum at 2247 or 2257 cm^{-1}. Frequencies characteristic of dienic (1625 cm^{-1}) and allenic (1965 cm^{-1}) groupings were very weakly represented in the spectra. Slight absorption in the 1700 cm^{-1} region is very frequently observed in the spectra of acetylenic compounds [7]. The ether grouping evidently corresponds to the 1100-1114 cm^{-1} doublet. In the 900-1000 cm^{-1} region all the spectra contain two intense bands at ~ 950 and 970 cm^{-1} and a weak band forming an overtone on a preceding band at ~ 917 cm^{-1}. The 917 and 970 cm^{-1} frequencies might be associated with the presence of a vinyl group in the bromoethers, although in the 1600-1640 cm^{-1} region and at 6100 cm^{-1} (overtone) the bromoethers do not exhibit the strong absorption characteristic of this group. The frequencies are most probably associated mainly with vibrations in saturated radicals.

Consequently, the infrared spectra confirm the earlier conclusions to the effect that alkyl hypobromites add on almost exclusively at the olefinic bond. At the same time they indicate that acetylenic bromoethers are not the sole products of the reaction: very small quantities of 1,3-dienic and allenic bromoethers are also formed.

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* Enynic systems. XXII.

Formation of a small quantity of allenic bromoethers was confirmed by the infrared spectra of the enolic ethers – products of dehydrobromination of the original bromoethers. These spectra contain a weak frequency at about 3300 cm^{-1} which is characteristic of the hydrogen of a terminal acetylenic grouping. Formation of an ether from such a grouping is only possible from an allenic bromoether according to the equation $R-COR=C=CH-CH_2Br \rightarrow R-COR=C=C=CH_2 \rightarrow R-COR=CH-C\equiv CH$.

The intensity of the 3300 cm^{-1} frequency falls off sharply on passage from vinylmethylacetylene to vinylethylacetylene, and is hardly perceptible in the higher homologs. Proof that the 3300 cm^{-1} frequency is associated with the stretching frequency of the acetylenic hydrogen is afforded by its disappearance after treatment of the enolic ethers with ammoniacal silver oxide. The enolic ethers are then recovered to the extent of over 90%. Consequently, the content of impurities must be much below 10%. A precipitate of silver derivative only comes down in the case of the enolic ether prepared from vinylmethylacetylene. Very slight turbidity is observed in other cases.

We effected addition of alkyl hypobromites to vinylalkylacetylenes by two methods: a) by the action of benzenedibromosulfonamide on alcoholic solutions of the hydrocarbons; b) by the action of a solution of bromine in methanol on a solution of the hydrocarbon in the same alcohol. The infrared spectra failed to reveal any significant differences in the structures of the resulting bromoethers. The second method gave compounds with excess of bromine due to the presence of a small quantity of dibromides.

EXPERIMENTAL

Methods of preparation of the hydrocarbons, their constants and the method of preparation of the bromoethers with the help of benzenedibromosulfonamide were described in previous communications [3, 4]. In this paper (see Table 1) we again present the constants of some of the bromoethers (since they were obtained in large quantities and the boiling point previously found for the bromoether from vinylpropylacetylene was erroneous [4]).

TABLE 1

Substance	Boiling point (10 mm)	d_4^{20}	n_D^{20}	MR_D	
				found	calc.
$CH_2Br-CH(OCH_3)-C\equiv C-CH_3$	65–66°	1.3647	1.4880	37.38	37.31
$CH_2Br-CH(OCH_3)-C\equiv C-C_2H_5$	77–78	1.2900	1.4804	42.11	41.93
$CH_2Br-CH(OCH_3)-C\equiv C-C_3H_7$	88–89	1.2415	1.4782	46.78	46.55
$CH_2Br-CH(OCH_3)-C\equiv C-C_4H_9$	105–106	1.2016	1.4758	51.42	51.17

The hydrocarbons were treated with an alcoholic solution of bromine under the following conditions.

A methanol solution of 0.2 mole bromine (cooled to −5 to −10°) was added dropwise with intensive stirring to a solution of 0.25 mole vinylethylacetylene in 100 ml alcohol (cooled to the same temperature). When the reaction was completed, the mixture was diluted with water, and the layer of bromoether was collected, washed with saturated $CaCl_2$ solution and distilled. There was obtained 25 g product which yielded the following fractions on distillation in vacuo (10 mm): 1st, to 76°, 1.5 g; 2nd, 76–78°, 16.8 g; 3rd, 78–80°, 5 g; 4th, 80–82°, 3 g; residue, 7 g. Yield of bromoether (fractions 2 and 3) 57%.

The main fraction had: d_4^{20} 1.3164, $n^{20}D$ 1.4848.

Found %: Br 44.33, 44.27. $C_7H_{11}OBr$. Calculated %: Br 41.92.

The analytical data indicate that the product is contaminated with about 10% of dibromide.

Treatment of the bromoether with alcoholic alkali gave the enol ether with the following constants: b. p. 53–54° (20 mm), d_4^{20} 0.8894, $n^{20}D$ 1.4685.

TABLE 2

Infrared Transmission Spectra of Bromoethers $CH_2Br-CH(OCH_3)-C\equiv C-R$ with the Following Values of R.

CH_3	C_2H_5	C_3H_7	C_4H_9
2294 strong	2288 * strong	2278 strong	2278 * strong
2268 strong	2269 strong	2257 strong	2257 strong
2247 strong	2247 strong	2237 * strong	2237 * strong
1965 v. weak	1965 v. weak	1965 v. weak	1965 v. weak
1709 weak	1715 weak	1710 weak	1695 weak
1626 weak	1609 weak	1608 weak	1605 weak
1456 strong	1456 strong	1460 strong	1466 strong
—	1377 strong	1381 strong	1377 * strong
1346 strong	1330 strong	1335 strong	1333 strong
1321 strong	1318 strong		—
1270 * med.	1270 * med.	1276 med.	1248 * med.
1209 strong	1206 strong	1206 strong	1206 strong
1163 strong	1156 * strong	1156 * strong	1156 * strong
1114 v. strong	1114 v. strong	1114 v. strong	1114 v. strong
1100 v. strong	1100 * v. strong	1100 * v. strong	1100 * v. strong
1038 strong	1039 strong	1039 strong	1040 strong
1012 strong	1006 strong	1006 strong	1006 strong
971 strong	974 strong	968 strong	971 strong
950 strong	950 strong	947 strong	947 strong
917 med.	—	917 weak	—
850 med.	888 med.	888 weak	—
821 med.	808 med.	826 weak	—
781 med.	777 med.	793 med.	781 med.
—	—	741 med.	734 med.

Note. Starred frequencies are overtones on other (stronger) frequencies.

Its specific gravity and refractive index are slightly higher than for the pure substance due to the pressure of bromide formed by dehydrobromination of dibromide which was contained in the original bromoether.

The infrared spectra were obtained with the IKS-2 spectrograph, using a lithium fluoride prism down to 5.5 μ and subsequently a sodium chloride prism. The thickness of the layer was 0.1 mm and less.

The spectra of the purified enolic ethers were closely studied in one of the preceding communications [8]. Data for the spectra of the bromoethers are presented in Table 2 and plotted in the diagram.

SUMMARY

1. A study of the infrared spectra confirmed the previous conclusion as to the preferential addition of alkyl hypobromites to vinylalkylacetylenes (by the action of benzenedibromosulfonamide on alcoholic solutions of the hydrocarbons) at the double bond.

2. It was shown that along with this main direction of the reaction, there is partial addition of alkyl hypobromites at the acetylenic bond and in the 1,4-position. With increasing size of the alkyl radical of the hydrocarbon, the last direction of the reaction becomes less pronounced.

3. It was established that the addition reaction goes in the same direction when bromine acts on alcoholic solutions of vinylalkylacetylenes.

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THE VAPOR-PHASE CATALYTIC HYDRATION OF ACETYLENE AND ITS HOMOLOGS

III. STUDY OF THE PROCESS OF CATALYTIC HYDRATION OF ACETYLENE OVER SOME SOLID CATALYSTS

Iu. A. Gorin and I. K. Gorn

Information on the hydration of acetylene to acetaldehyde in the gas phase over solid catalysts has been supplied mainly by the patent literature without any discussion of theoretical considerations that might enable correlation of the activity of the catalysts with their nature and properties. The lack of such data must be attributed to the empirical basis of selection of the majority of the catalysts put forward in patents. There has been an entire lack of systematic work. Of the large number of substances proposed, we can only mention some of the more common ones: phosphoric acid and various phosphates (in particular copper phosphate , zinc phosphate and cadmium phosphate), sometimes other salts of the same metals, and compounds of tungsten, molybdenum and vanadium [1-3]. The mechanism of the hydration of acetylene over solid catalysts has been very inadequately investigated, although an insight into this mechanism might be expected to facilitate the correct choice of catalyst. There are only a few publications dealing with the fundamentals of this reaction, and they do not contain any detailed considerations.

Boswell and Dilworth [4] studied the catalytic action of alumina in a number of hydration and dehydration reactions (including the hydration of acetylene) and attribute the effect to surface films of ions of dissociated water which cover the catalyst particles. Iakubovich and others [5] studied the activating effect of phosphates of zinc and copper on phosphoric acid supported on active carbon. They apparently suggested that the copper salt activates the process when it is in a state of higher valence since they consider the reduction to the lower valence stage to be one of the possible causes of deactivation of the catalysts during the reaction. They found the lower oxide in the spent catalyst.

An insight into the mechanism of the reaction at solid catalysts can be obtained from the ideas propounded by some investigators on the liquid-phase process. A. L. Klebanskii and V. D. Titov [6] investigated the hydration of acetylene in phosphoric acid solution in presence of salts of zinc, silver and mercury; they attribute the activating action of these salts to their ability to form complexes with acetylene, the molecule of the latter becoming activated on ionization of the complex. The authors emphasize that the activating action of such salts is especially conspicuous when the reaction is conducted in the vapor phase on solid supports. The theory of Klebanskii and Titov is an interesting one since the nature of the activation of acetylene may be the same in the conditions of liquid-phase and gas-phase hydration. The actual occurrence of ionization of acetylene in solutions under the action of lower copper salts was subsequently confirmed by the work of A. L. Klebanskii, I. M. Dolgoplosk, and Z. F. Dobler [7, 8]. The authors associate the ready susceptibility of acetylene to ionization with the mobility of the π-electrons of the triple bond.

In the present work we studied the hydration of acetylene over solid catalysts containing various cations, since the development of cations capable of activating the reaction can serve as a first step toward the understanding of the mechanism of action of a catalyst. In order to exclude the influence of anions, we used only phosphates as catalyst. Along with this we investigated the catalytic action of some of those metals whose phosphates were found to be active catalysts.

Special Features of the Electronic Structure of Phosphates Capable of Catalyzing the Hydration of Acetylene

Of the very large number of phosphates (neutral orthophosphates) only a few are capable of catalyzing the hydration of acetylene, namely the phosphates of copper, cadmium and zinc. A number of other phosphates are characterized by extremely low activity or by substantial absence of activity. Our experimental results are presented in the table (Nos. 1-10).

Activity of Some Phosphates as Catalysts of the Hydration of Acetylene to Acetaldehyde

No.	Phosphate cation	Temperature	Degree of conversion of acetylene (in %)	Yield of acetaldehyde (mole%)	
				on acetylene passed through	on acetylene converted
1	Copper (ic)	250—300°	88.0	55.7	63.2
2	Cadmium	390—400	73.8	62.0	83.8
3	Zinc*	390—400	52.2	48.3	92.7
4	Calcium	390—400	3.3	1.2	—
5	Strontium	390—400	0.0	0.0	—
6	Barium	390—400	1.6	0.0	—
7	Aluminum	390—400	0.0	0.0	—
8	Iron (ic)	390—400	6.1	1.3	—
9	Nickel	390—400	6.0	4.2	—
10	Tin	390—400	0.0	0.0	—
11	Mercury (20 wt.% of mercuric phosphate on calcium phosphate)	320—330	4.8	2.4	—
12	Silver (20 wt.% of silver phosphate on calcium phosphate)	200—300	6.7	2.6	—
13	Silver (phosphate)	200—300	44.6	35.2	78.8

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* The catalytic properties of zinc phosphate were previously studied by Iu. A. Gorin, A. N. Makashina and others [9].

Phosphates of copper, cadmium and zinc differ in respect to the nature of their catalytic action. The overall catalytic activity of copper phosphate, determined from the degree of conversion of acetylene, is so high that hydration of acetylene proceeds in its presence at a relatively low temperature. At the same time the catalyst has poor selectivity, the yield of acetaldehyde (reckoned on reacted acetylene) being low, since secondary reactions play an important part (condensation of acetaldehyde to crotonaldehyde and oily products, and polymerization of acetylene to cuprene). The polymers are the cause of the rapid choking of the reaction tube.

Cadmium phosphate is less active than copper phosphate, the hydration of acetylene over $Cd_3(PO_4)_2$ requiring a higher temperature (reaction starts at 330-350°), although this catalyst is very much more selective and is more stable.

The least active of the three catalysts is zinc phosphate. It is evident that the difference in behavior of the phosphates during hydration of acetylene must be governed by the character of their cations. From this standpoint the cations of the phosphate which are active catalysts must possess some property in common. We established such a general property in the structure of the electron shells of the elements Cu, Zn and Cd [10]. In each of these elements one or two of the electrons of the s subgroup are in the outer shell. The d subgroup of the preceding (penultimate) orbital is then completely filled by ten electrons (Cu – $3d^{10}4s$, Zn – $3d^{10}4s^2$, Cd – $4d^{10}5s^2$). To the same elements whose d subgroup is not completely filled, even when the outer shell contains s-electrons, correspond phosphates which are characterized by low activity in the hydration of acetylene, as can be seen with reference to the phosphates of iron and nickel (Fe – $3d^6 4s^2$, Ni – $3d^8 4s^2$). d-Electrons are also absent from the vicinity of the outer s-electrons in the elements Al, Ca, Sr, Ba (Al – $3s^2 3p$, Ca – $3p^6 4s^2$, Sr – $4p^6 5s^2$, Ba – $5p^6 6s^2$), and this structure likewise coincides well with the absence of catalytic activity from their phosphates. It is true that in the salts we are not dealing with atoms of Cu, Cd or Zn, but with ions; nevertheless the completion of the number of electrons of the d subgroup is evidently the decisive factor.

On the other hand, subsequent filling of the outer orbital with electrons (appearance of p-electrons) also leads to loss of activity, as is observed in the case of tin phosphate (Sn – $4d^{10}5s^2 5p^2$).

The above-noted feature of the structure of the outer orbitals of the electron shell characteristic not only of Cu, Cd and Zn, but also of Ag, Au and Hg (Ag – $4d^{10}5s$, Au – $5d^{10}6s$, Hg – $5d^{10}6s^2$). There are no other elements of similar structure in the periodic system. It was therefore of interest to compare the catalytic action in acetylene hydration of phosphates of these elements with the action of phosphates of copper, cadmium and zinc. Since the literature contains no information about the possibility of preparation of gold phosphates, we studied the catalytic properties of only mercury and silver phosphates (table, Nos. 11-13).

For convenience in testing, we used mercuric phosphate in admixture with calcium phosphate which served as a carrier.* During the reaction it was completely reduced to metallic mercury which condensed in the cold part of the reaction tube.

Silver phosphate was tested both in admixture with a carrier (calcium phosphate) and in its absence. It, too, suffered decomposition, as was especially conspicuous in experiments in which silver phosphate was used alone (the spent catalyst consisted of free phosphoric acid and metallic silver). It should be pointed out that decomposition of silver phosphate was avoided by starting the test in both cases at low temperature (200°), and only in the event of complete inertness of the catalysts was the temperature gradually raised to 300°. The reaction only commenced at 285° when silver phosphate was used without a carrier ; substantially no conversion of acetylene was observed when silver phosphate was mixed with calcium phosphate.

The lack of activity of mercuric phosphate can be easily explained by the reduction to mercury which, as we know from the liquid-phase process, does not catalyze the hydration of acetylene. From this standpoint the catalytic effect of silver phosphate alone (which is likewise reduced to metal) is anomalous. This anomaly, however, is only an apparent one, for the catalytic effect must here be attributed to the phosphoric acid which is liberated on breakdown of the phosphate. Catalysts were found to be inert when the conditions were such that free phosphoric acid could not be present. This would apply in presence of a carrier (calcium phosphate, with which phosphoric acid reacts to form the catalytically inert pyrophosphate). Decomposition of the phosphate evidently only occurs at about 285°, for otherwise the commencement of reaction would have been observed at a lower temperature since phosphoric acid catalyzes the hydration of acetylene even at 130° [6]. Silver phosphate itself is evidently inactive at temperatures below 285°. These observations show that silver phosphate is scarcely suitable as a solid catalyst for the hydration of acetylene.

We checked the lack of catalytic activity of free metals in acetylene hydration in the case of zinc and cadmium. Zinc was tested at 390-400° in the form of dust pelleted with pulverized pumice. Whereas zinc phosphate is an active catalyst, the degree of conversion of acetylene in presence of zinc under the same conditions was only 6.9%.** Metallic cadmium was tested in the form of dust at a lower temperature than was employed with zinc (the melting point of cadmium is 320.9°) and was likewise inactive. The inability of the free metals to catalyze the hydration of acetylene indicates that the reaction of the solid catalyst with acetylene has an ionic character. In view of the suggested possibility of formation of complexes of acetylene with copper salts in solutions [7], we suggest that ions of copper, cadmium and zinc in the solid catalyst lattice form complexes with acetylene at the catalyst surface at the expense of the π-electrons of the triple bond.

In an earlier communication [12] we proposed the mechanism of hydration of acetylene and some of its mono- and disubstituted derivatives which is based on the results and concepts obtained and developed in the present work. Formation of complexes necessary for activation of acetylene hydration evidently proceeds only when the electron cloud of the cations of the catalyst has a specific structure, and this structure also characterizes the three cations in question. This is equally true of the mercury cation. It is true that mercuric phosphate cannot be used as a gas-phase catalyst due to its great susceptibility to reduction to metal under the reaction conditions, but mercury salts are generally known to be active in the liquid-phase process.

In this connection it is highly probable that only bivalent cations can activate the hydration of acetylene. This is not so, for example, in the case of its polymerization. This view is supported by the well-known fact that mercurous salts do not catalyze this reaction in the liquid phase. One of us [13] has drawn attention to the poor activity of solid catalysts containing cuprous salts. It may be thought that a condition for formation of complexes capable of activating the hydration of acetylene both in solutions and on solid catalysts is the presence of a charge of specific magnitude on the cations along with the above-mentioned structure of the electron cloud. When the charges are lower, i. e., in the case of univalent cations, the required degree of polarization or ionization of acetylene is not attained. On this basis the silver cation cannot activate the hydration of acetylene even if we ignore the facility of breakdown of silver phosphate.

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* Calcium phosphate has been employed as a good carrier for various acetylene hydration catalysts [11].

** The slight activity of zinc was probably due to formation of some zinc oxide which is known to catalyze the hydration of acetylene.

If the ideas that we have put forward about the relation between a specific structure of the electron cloud of cations and the ability of the salts of these cations to activate the hydration of acetylene are correct, then it follows that the number of suitable catalysts (salts) is indeed very small. Grave doubt must therefore be cast upon the claims in patent literature for the suitability as catalysts of numerous salts with other cations.

EXPERIMENTAL

Phosphate catalysts were prepared by precipitation from solutions of the corresponding sulfates or nitrates by the action of solutions of di- or trisubstituted ammonium orthophosphate. The precipitates were filtered, washed free of soluble salts, dried at 100-110° and compressed to tablets in a laboratory hydraulic press. The tablets were then broken into 2-3 mm pieces. Mixed catalysts (silver phosphate or mercuric phosphate mixed with calcium phosphate) were prepared by mechanical mixing of the separately precipitated phosphates which had been pulverized and sieved through a 0.15 mm-mesh screen. Mixing was effected in suspension in water. The mixture was then filtered, dried and tableted. The catalyst consisting of zinc dust and pumice was prepared by mixing the powders in the dry state and then tableting. The cylinder acetylene employed in the tests was purified by washing with sodium hypochlorite solution. After purification, the gas contained 98% acetylene (determination by absorption in oleum).

Acetylene was hydrated in a quartz tube, diameter 25 mm and length 1 m, heated in an electric furnace. The amount of catalyst was 50 ml; the remaining space in the reaction tube was filled with pieces of quartz. Acetylene was admitted into the furnace from a gas-holder via a flowmeter, and water from a small buret. Reaction temperatures were measured with a thermocouple whose junction was in the center of the catalyst bed. The reaction products passed through a water condenser and were collected in a receiver cooled with ice. The gas, consisting mainly of unreacted acetylene, was washed free of aldehyde vapor in absorption bulbs containing hydroxylamine and collected in a gas-holder. The temperature of the experiments was usually 390-400°, the space velocity 150 liters/liter cat./hr, the dilution (by volume) of the acetylene with water vapor 1 : 10. Duration of the experiments 3-5 hrs. Aldehyde and aqueous-acetylenic condensate were determined with hydroxylamine hydrochloride. Unreacted acetylene in the gaseous reaction products was determined by absorption in oleum.

SUMMARY

1. Several salts of phosphoric acid with various cations, as well as metallic zinc and cadmium, were examined as catalysts for the gas-phase hydration of acetylene to acetaldehyde.

2. It was shown that the action of solid catalysts of acetylene hydration bears an ionic character.

3. It was shown that the phosphate cations (Cu, Cd, Zn, Hg) which catalyze the hydration of acetylene are characterized by a specific structure of the electron cloud. Deviation from this structure involves loss of catalytic activity in this reaction.

4. The theory is advanced that activation of the hydration of acetylene is achieved only by bivalent cations.

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INVESTIGATIONS ON POLYMETHYLENE RINGS

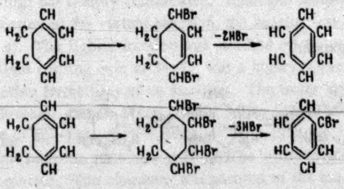
XXXII. TRANSFORMATIONS OF CYCLOHEXENE IN CONJUGATED HALOGENATIONS AND DEHALOGENATIONS

N. A. Domnin and V. A. Cherkasova

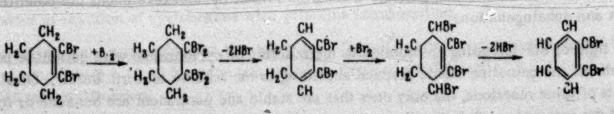
We have shown in a series of investigations that 1,3-cyclohexadienes and their substituted derivatives, likewise polyhalo derivatives of cyclohexane, are converted to the corresponding aromatic compounds under conditions of conjugated halogenation and dehalogenation [1]. Characteristic of these conversions is their irreversibility with formation of stable aromatic end products. These transformations are therefore analogous with Zelinskii's "irreversible catalysis."

Another characteristic feature of these transformations is the necessary presence of a source of bromine, which can be molecular bromine itself or a quoline polybromide, tetrabromo- and hexabromoethanes and other compounds rich in bromine and releasing it with facility.

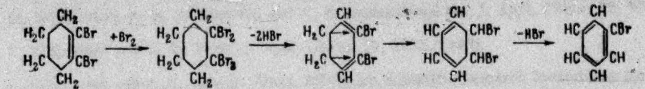
We advanced a mechanism of conjugated halogenation and dehalogenation based on investigation of these reactions. Two variants were suggested: transformations with a relatively simple mechanism involving addition and scission of halogens or hydrogen halides, and transformations accompanied by intramolecular isomerizations. The first variant may be represented by the simplest conversion of 1,3-cyclohexadiene into benzene and bromobenzene in presence of polybromides of quinoline or of hexabromomethane and quinoline.



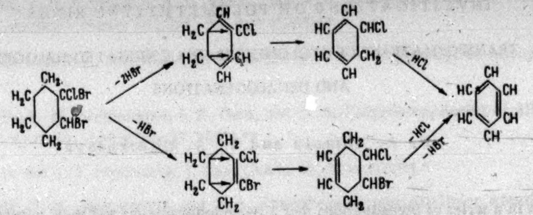
Another example is the conversion of 1,2-dibromo-1-cyclohexene into o-bromobenzene under the action of molecular bromine.



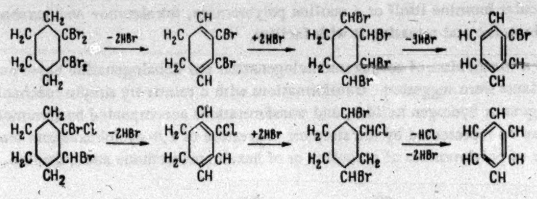
The second variant can be illustrated by the transformation of 1,2-dibromo-1-cyclohexene into bromobenzene under the action of bromine.



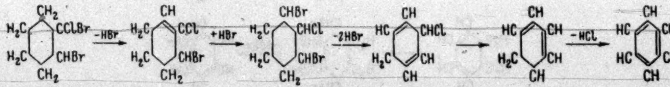
Another example is the transformation of 1-chloro-1,2-dibromocyclohexane into benzene under the action of quinoline.



The mechanism of the first type of conversion can be considered proven, but that of the second type has remained unproven, since the migration of hydrogen atoms to the β-position has hitherto not been demonstrated. We can therefore advance another mechanism for the second type of conversion which involves cleavage and subsequent addition of hydrogen halide according to the scheme:

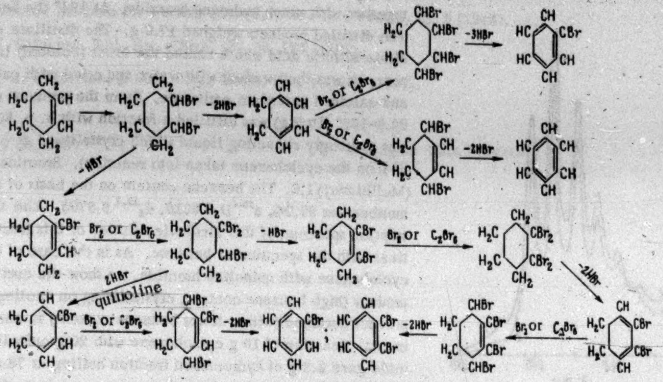


or a subsequent allylic rearrangement:



The above mechanisms of conjugated halogenation and dehalogenation take account of all of the known facts in this field. It must be remembered that there is a possibility of these reactions proceeding simultaneously in accordance with all of the suggested schemes. In connection with the further study of the mechanism of these reactions, it was of interest to investigate the transformations of cyclohexene under the conditions of conjugated halogenation and dehalogenation.

In the light of the foregoing considerations the reaction of cyclohexene with quinoline polybromides or of hexabromoethane and quinoline should proceed according to the scheme set forth below. Of all of the possible main products of these reactions, the only ones that are stable and permanent are benzene or its halogenated derivatives. All of the remainder – 1-bromo-1-cyclohexene, 1,2,2-tribromocyclohexene, 1,2-dibromo-1-cyclohexene, and 2-bromo-1,3-cyclohexadiene – will be intermediates and are most probably converted into bromobenzene and o-dibromobenzene or into benzene. Experiment confirmed this supposition. Benzene is formed when cyclohexene reacts with quinoline tetrabromide or with hexabromoethane in presence of quinoline.



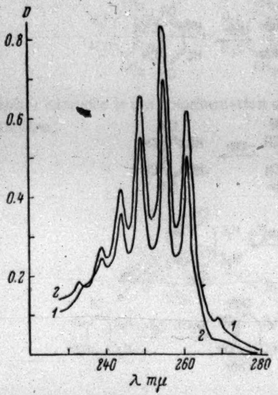
EXPERIMENTAL

Reaction of cyclohexene with quinoline dibromide. Cyclohexene was prepared [2] by the action of sulfuric acid on cyclohexane. After careful fractionation, a fraction with b. p. 83-83.5° was selected. Quinoline dibromide was prepared from quinoline supplied by the Kharkov Chemical Reagent Works, serial number 50/28.

40 g quinoline dibromide was added through a reflux condenser to 8 g cyclohexene in a round-bottomed flask. The contents of the flask formed layers. The top layer was collected (20 g). It was the hydrate water of quinoline dibromide remaining after reaction of the dibromide with cyclohexene. A further small quantity of oil came down when water was added to the top layer. The oil was added to the main product (the lower layer). The latter was a brown, heavy oil (28 g), consisting of 1,2-dibromocyclohexane in quinoline. The oil was washed with water, dried with calcined potassium carbonate, and then heated in a round-bottomed flask to which a reflux condenser was attached. A violent reaction ensued at 170° (temperature in the flask); subsequently the contents of the flask formed two layers, though not sharply demarcated. Hydrogen bromide was copiously evolved from the reaction mixture. After completion of the violent reaction, the heating was continued and a fraction with b. p. 74-150° was collected (19.4 g). The lighter fraction was distilled off (prior to this the contents of the flask copiously evolved HBr); the distillate coming over at 74-75° was a highly refractive liquid. The amount collected up to 110° was 3.7 g. The fraction formed layers on standing. The lower layer reacted with calcined potassium carbonate with heat evolution and release of gas. After careful drying, distillation gave a fraction of 3.7 g (48.5%) with b. p. 80.5-81.5°; it crystallized at −10°; $d_4^{13.7}$ 0.8762, $n^{13.7}D$ 1.4978; McIlhinney bromine number [3] 7.72. Judging by the bromine number, the benzene content was 96%. The ultraviolet absorption spectrum of the alcoholic solution of this fraction was plotted. The character and position of the maxima are identical with those of benzene. We were more interested, however, in the spectrum of the product containing less benzene; we therefore show two curves for this material, plotted with the help of the SF-11 spectrophotometer. These relate to the product of interaction of 10.2 cyclohexane with 43 g quinoline dibromide, obtained in the final 3 g of 78.5-81° fraction, $n^{20.9}D$ 1.4711, $d_4^{20.9}$ 0.8416. Curve 1 relates to a 0.1% alcoholic solution of this product (curve 2 corresponds to the product of reaction of cyclohexene with quinoline tetrabromide).

Reaction of cyclohexene with quinoline tetrabromide. Quinoline tetrabromide was prepared by Grimaux's method [4] (slightly modified) – 12 ml bromine was added to a cooled emulsion of 15.2 g quinoline in 45 ml water. It was used without recrystallization.

20 g quinoline tetrabromide was added portionwise through a reflux condenser to 10 g freshly distilled cyclohexene. Layer formation took place: the upper layer was nearly colorless and the lower layer dark. A further 14.3 g tetrabromide was added; nearly the whole of this dissolved. The layers were separated. The upper (aqueous) layer weighed 9.3 g. When mixed with water it deposited a further small quantity of yellow oil. The lower layer (31.2 g) was transferred to a Wurtz flask and cautiously heated. Reaction commenced at 170° (temperature in the



Ultraviolet absorption curves (see text for explanation).

liquid). At 142° a fairly light-colored fraction started to come over together with much hydrogen bromide. At 184° the heating was stopped. The distilled products weighed 17.6 g. The distillate was washed with dilute sulfuric acid which caused the lower (colored) layer to disappear; it was then washed with water and dried with calcium chloride and calcined potassium carbonate. From the products collected at 80.5-160° (10.2 g) was distilled a fraction with b. p. 80.2-82°; this was a strongly refracting liquid which crystallized at −5° (5.8 g or 61% on the cyclohexene taken into reaction). Bromine number (McIlhinney) 1.6. The benzene content on the basis of the bromine number was 99.2%, $n^{19.4}D$ 1.5016, $d_4^{19.4}$ 0.8795. The ultraviolet absorption spectrum of the alcoholic solution of this fraction was identical with the spectrum of benzene. As in the case of interaction of cyclohexene with quinoline bromide, we show the curve not of this product (high benzene content, crystallizing on cooling) but of the product obtained (with a lower benzene content) in one of the experiments. Reaction of 10 g cyclohexene with 20 g quinoline tetrabromide gave 6.3 g of hydrocarbon fraction boiling at 78.5-82°, $n^{20.5}D$ 1.4688. The ultraviolet absorption spectrum, taken with the ISP-22 spectrograph, indicated the presence of benzene (4 benzene maxima are visible on the spectrogram). From the 78.5-81° fraction was distilled a portion with b. p. 80.5-82°, $n^{21}D$ 1.4667, d_4^{21} 0.8377; the absorption curve of the 0.1% alcoholic solution, taken with the SF-11 spectrophotometer, is given in the diagram (curve 2).

Vacuum distillation of the heavy oil (residue from the fraction crystallizing on cooling with b. p. 80.5-82° and $n^{19.4}D$ 1.5016) gave a fraction with b. p. 97-98° at 10 mm (7.8 g), $n^{19.4}D$ 1.5520, M 231. Calculated for 1,2-dibromocyclohexane: M 242; for bromocyclohexene: M 159.

Interaction of cyclohexene with hexabromoethane and quinoline. 13 g freshly distilled quinoline was added to 50.3 g hexabromoethane (obtained by Gustavson's method [5]) in a flask with a reflux condenser topped by a calcium chloride tube. 8.2 g cyclohexene was run into the resulting viscous mass through a dropping funnel (strong cooling was observed during this operation). The contents of the flask were heated on an oil bath at 150-155° for 3.5 hrs. The reflux condenser was replaced by an Anschütz fitting, and a wide fraction in the 80-220° range was distilled off (30.7 g). Considerable evolution of hydrogen bromide occurred at the same time. Most of the distillate came over at 80-120°. The mass was washed with dilute sulfuric acid (the quantity of oily product was reduced by this treatment to 24 g), then with water, and dried. Subsequent distillation gave 11.5 g of slightly cloudy liquid in the 78-158° range. Fractionation at atmospheric pressure from a Favorskii flask gave a fraction with b. p. 78-83° (4.5 g or 57.5% on the cyclohexene taken into reaction). A small quantity of bromine remained in the fraction (Beilstein test) in spite of careful purification. Our determinations of the constants – $d_4^{18.2}$ 1.0253 and $n^{18.2}D$ 1.4977 – also indicated the presence of a bromide; the bromine number of 7.28 (McIlhinney) corresponded to a benzene content of about 97%. The product did not crystallize when cooled to −5°. The ultraviolet absorption spectrum of the alcoholic solution was taken with the ISP-22 spectrograph. The position and character of the five maxima on the spectrogram coincided with those of benzene.

SUMMARY

1. Cyclohexene, the more saturated isolog of 1,3-cyclohexadiene, is capable like the latter of transformation into an aromatic system under the conditions of the reaction of conjugated halogenation and dehalogenation.

2. Heating of cyclohexene with quinoline polybromides (either the dibromide or the tetrabromide) as well as with hexabromoethane in presence of quinoline causes a considerable proportion to be converted to benzene (46.57, 60.51 and 55.78%, respectively).

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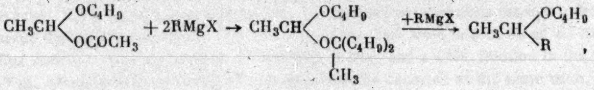
INVESTIGATION OF THE EXCHANGE OF OXY RADICALS FOR THE HYDROCARBON RADICALS OF ORGANOMAGNESIUM COMPOUNDS

IV. INTERACTION OF GRIGNARD REAGENTS WITH ORGANIC ACYLALS

M. F. Shostakovskii and M. R. Kulibekov

In our preceding communications [1] we studied the exchange of oxy radicals of organic and organosilicon acetals for radicals of organomagnesium compounds. It was established that heavier oxy radicals are more readily replaced. In the case of organosilicon acetals the oxy radical that is usually replaced is one containing a silicon atom.

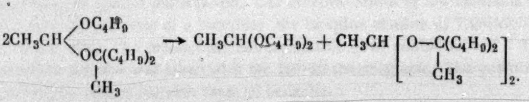
The present investigation was devoted to the interaction of a Grignard reagent with organic acylals. We know from the literature [2] that acylals are not susceptible to the symmetrization reaction, although they readily exchange their acyl group for an alkoxy radical. It was of interest to study the behavior of acylals in reactions with organomagnesium compounds. In the case of reaction of a series of organomagnesium compounds with butoxyethylidene acetate, we showed that the Grignard reagent initially reacts with the carbonyl group of the acylals to form a mixed acetal of a tertiary alcohol, which in turn again reacts with the organomagnesium compound and exchanges the residue of the tertiary alcohol for an organic radical according to the scheme



$$CH_3CH\left\langle\begin{matrix}OC_4H_9\\OCOCH_3\end{matrix}\right. + 2RMgX \rightarrow CH_3CH\left\langle\begin{matrix}OC_4H_9\\O\underset{\substack{|\\CH_3}}{C}(C_4H_9)_2\end{matrix}\right. \xrightarrow{+RMgX} CH_3CH\left\langle\begin{matrix}OC_4H_9\\R\end{matrix}\right. ,$$

where R = H, C_4H_9, $C_6H_5CH_2$, C_6H_5; X = Cl or Br.

In addition we established that a certain proportion of the acetal undergoes symmetrization during the process with formation of two acetals:



$$2CH_3CH\left\langle\begin{matrix}OC_4H_9\\O\underset{\substack{|\\CH_3}}{C}(C_4H_9)_2\end{matrix}\right. \rightarrow CH_3CH(OC_4H_9)_2 + CH_3CH\left[O-\underset{\substack{|\\CH_3}}{C}(C_4H_9)_2\right]_2.$$

The transition from acylals to mixed acetals of tertiary alcohols and the symmetrization of the latter have not been discussed in the literature. These reactions can evidently serve for the synthesis of mixed acetals with primary and tertiary radicals.

The butyl ether of methylbenzylcarbinol synthesized by us has a delicate floral odor whose aromaticity is not inferior to that of β-phenylethyl alcohol.

EXPERIMENTAL

1. Reaction of ethylidene acetate with butyl magnesium bromide. To the Grignard reagent prepared from 4 g magnesium and 23 g butyl bromide was added 15 g butoxyethylidene acetate at room temperature with stirring.

The mixture was then heated for 2 hrs at 35-36° and treated (with cooling) with 5% acetic acid. The ethereal layer was collected, washed with 5% sodium carbonate solution and then with water, and dried over sodium sulfate. The ether was taken off and the residue fractionated to give the following products:

4.07 g butyl ether of methylbutylcarbinol with b. p. 53-54° at 4 mm, $n^{20}D$ 1.4100, d_4^{20} 0.7884, MR_D 49.88, calc. 50.02.

1.61 g dibutylacetal [3] and 2.88 g mixed acetal of butyl alcohol and methyldibutylcarbinol with b. p. 79-80° at 6 mm, $n^{20}D$ 1.4156, d_4^{20} 0.8200, MR_D 78.89; calc. 79.39. Found %: C 74.27, 74.07; H 13.66, 13.65. $C_{16}H_{34}O_2$. Calculated %: C 74.42; H 13.18.

Also isolated were 1.56 g methyldibutylcarbinol [4] with b. p. 86-87° at 5 mm, $n^{20}D$ 1.4330, d_4^{20} 0.8305; and 2.02 g symmetrical acetal of methyldibutylcarbinol with b. p. 93-95° at 5 mm, $n^{20}D$ 1.4239, d_4^{20} 0.8132, MR_D 107.30, calc. 107.08. Found %: C 76.81, 77.02; H 14.05, 13.95. $C_{22}H_{46}O_2$. Calculated %: C 77.19; H 13.46.

The symmetrical acetal of methyldibutylcarbinol is a transparent liquid with a pleasant odor, insoluble in water, easily soluble in organic solvents.

2. Reaction of butoxyethylidene acetate with benzyl magnesium chloride. The procedure followed the same lines as that in the preceding reaction. Starting components were 6 g magnesium, 31.6 g benzyl chloride and 15 g butoxyethylidene acetate. The following were obtained:

5.7 g butyl ether of methylbenzylcarbinol (a liquid with a pleasant floral odor) with b. p. 89-89.2° at 22 mm, $n^{20}D$ 1.4873, d_4^{20} 0.9109, MR_D 60.71; calc. 60.28. Found %: C 81.74, 81.64; H 10.20, 10.10. $C_{13}H_{20}O$. Calculated %: C 81.26; H 10.40.

5.75 g methyldibenzylcarbinol with b. p. 153-156° at 2.5 mm, $n^{20}D$ 1.5578, d_4^{20} 1.0381, MR_D 70.27; calc. 70.41. Found %: C 84.35, 84.56; H 8.25, 8.36. $C_{16}H_{18}O$. Calculated %: C 84.83; H 7.97.

3. Reaction of butoxyethylidene acetate with phenyl magnesium bromide. 12.5 g butoxyethylidene acetate was added to phenyl magnesium bromide prepared from 4 g magnesium and 26 g bromobenzene. This synthesis gave:

4.54 g methylphenylcarbinol [5] with b. p. 118-119.5° at 9 mm, $n^{20}D$ 1.4838, d_4^{20} 0.9101; and 2.59 g 1,1-diphenylethylene with b. p. 127-128° at 9 mm, $n^{20}D$ 1.5968, d_4^{20} 1.0326. The constants agree entirely with those reported in the literature [6].

SUMMARY

1. The reaction of butoxyethylidene acetate with Grignard reagent was investigated. It was shown that reaction occurs at the carbonyl acyl group with formation of the corresponding mixed acetals. The mixed acetals in turn enter into exchange reaction with the Grignard reagent to form the corresponding butyl ethers.

2. The mixed acetal of butyl alcohol and methyldibutylcarbinol is susceptible to symmetrization.

3. Methyldiphenylcarbinol, formed during the exchange reaction of the corresponding mixed acetal, easily undergoes dehydration under the reaction conditions and forms 1,1-diphenylethylene.

4. The following were synthesized for the first time: mixed acetal of butyl alcohol and methyldibutylcarbinol, ditertiary acetal of methyldibutylcarbinol, methyldibenzylcarbinol, and the butyl ether of methylbenzylcarbinol.

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Agriculture

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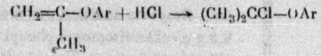
SYNTHESIS AND TRANSFORMATIONS OF α-SUBSTITUTED VINYL ETHERS

VII. SYNTHESIS AND TRANSFORMATIONS OF α-CHLOROISOPROPYL ARYL ETHERS

M. F. Shostakovskii, E. P. Gracheva, and N. K. Kul'bovskaia

In the present work we studied the synthesis of α-chloroisopropyl aryl ethers prepared by hydrochlorination of α-methylvinyl aryl and α-methylvinyl cyclohexyl ethers. Their properties were also studied. The following were prepared for the first time; α-chloroisopropyl phenyl, and the corresponding m-cresyl, guaiacyl and cyclohexyl ethers by the reaction

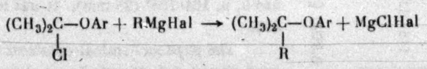


$$CH_2{=}\underset{CH_3}{\underset{|}{C}}{-}OAr + HCl \longrightarrow (CH_3)_2CCl{-}OAr$$

According to the literature [1], the α-chloroisopropyl alkyl ethers are extremely unstable and quickly break down to alkyl chloride and acetone. The α-chloroethers $CH_3{-}CHCl{-}OAr$, described by one of us [2], are more stable than α-chloroisopropyl aryl ethers. The latter break down when distilled; they blacken when stored for 2-3 hrs; they can be kept longer in solution in diethyl ether. α-Chloroisopropyl aryl ethers can be arranged in the following order of stability: α-chloroisopropyl phenyl > m-cresyl > guaiacyl > cyclohexyl.

Due to their instability on distillation, the prepared α-chloroisopropyl aryl ethers were characterized by various chemical reactions. Hydrogen halide and acetone were determined nearly quantitatively after hydrolysis. With excess of alcoholic alkali the expected alkyl phenyl ketal gives breakdown products – α-methylvinyl alkyl ether and phenol. Potassium phenoxide reacts to give diphenyl ketal in low yield.

α-Chloroisopropyl aryl ethers are of interest as starting substances for preparation of the little studied tert-alkyl aryl ethers.



$$(CH_3)_2\underset{Cl}{\underset{|}{C}}{-}OAr + RMgHal \longrightarrow (CH_3)_2\underset{R}{\underset{|}{C}}{-}OAr + MgClHal$$

A few members of this series of ethers have been described in the literature [3]. We prepared tert-butyl phenyl, tert-amyl phenyl, 1,1-dimethylbutyl phenyl, tert-amyl m-cresyl ethers. They are colorless liquids with a pleasant odor; when boiled they rearrange to the corresponding tert-alkyl phenols [4].

EXPERIMENTAL

The starting α-methyl-substituted vinyl ethers were prepared by the method previously described [5].

Synthesis of α-chloroisopropyl phenyl ether. 35 g α-methylvinyl phenyl ether (b. p. 61-69° at 16 mm, $n^{20}D$ 1.5048) was put into a three-necked flask fitted with thermometer, stirrer and reflux condenser (the latter topped by a calcium chloride tube). A stream of dry hydrogen chloride was introduced with stirring and cooling to −20°, the speed being so regulated that the temperature did not rise above −10°. The reaction was continued to full saturation in the couse of 3 hrs. The solution then had a brown color. (Reaction in diethyl ether gives a product with a lighter color.) Without the temperature being raised above 0°, the excess of hydrogen chloride was purged out with a stream of dry nitrogen; the increase in weight was 10.6 g (instead of 10.7). The α-chloroether was used in various reactions in the undistilled form. In similar fashion we prepared α-chloroisopropyl m-cresyl, α-chloroisopropyl guaiacyl and α-chloroisopropyl cyclohexyl ethers.

Hydrolysis of α-chloroisopropyl phenyl ether. An ampoule containing a weighed sample of the ether (0.5-0.7 g) was placed in an Erlenmeyer flask with a ground glass stopper, containing 50 ml distilled water. The ampoule was crushed, and the solution was mixed for about an hour on a shaker. The resulting acid was titrated with 0.1 N caustic alkali in presence of methyl orange [2]. Found: 97.6-98.1% of titrated hydrochloric acid. After the titration of the acid, 70 ml of 0.5 N hydroxylamine hydrochloride solution was added and the acetone content was determined. Found in the hydrolyzate: 98.5, 98.8% acetone. Similar hydrolyses were performed on α-chloroisopropyl m-cresyl, guaiacyl and cyclohexyl ethers. Found: 98-99% of titratable hydrochloric acid and 98.5-99% acetone.

Reaction of α-chloroisopropyl phenyl ether with butanol. A solution of sodium alkoxide, prepared by reacting 2.93 g Na with 14.82 g anhydrous butyl alcohol, was charged into a three-necked flask fitted with stirrer, thermometer, condenser and dropping funnel. Dropwise addition was made (with cooling to −3 to −5°) of 8.3 g α-chloroisopropyl phenyl ether. The precipitate of sodium chloride (2.7 g) was filtered off and the filtrate was distilled to give 3.9 g phenol and 0.5 g α-methylvinyl butyl ether; b. p. 113°, $n^{20}D$ 1.4118 [6].

Reaction of α-chloroisopropyl phenyl ether with ethyl magnesium bromide. Dropwise addition of 36 g α-chloroisopropyl phenyl ether was made to an equimolar quantity of ethyl magnesium bromide prepared from 22.9 g C_2H_5Br and 5.1 g Mg in a flask equipped with condenser, stirrer and thermometer. The solution was stirred 2 hrs and left overnight. The mixture was decomposed with 10% H_2SO_4 in ether. The ethereal layer was collected, washed with water and caustic alkali for removal of phenolic products, dried with potassium carbonate, and distilled in vacuo. There was obtained 14.2 g of a fraction with b. p. 98-103° (28 mm), which after redistillation had b. p. 104-105° (28 mm); it was tert-amyl phenyl ether; yield 40%.

The physicochemical constants of tert-butyl phenyl, tert-amyl phenyl, 1,1-dimethylbutyl phenyl and tert-amyl m-cresyl ethers, prepared by the above procedure, are listed in the table.

Name of compound	Yield (%)	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D		Found (%)		Empirical formula	Calculated (%)	
					found	calc.	C	H		C	H
Tert-butyl phenyl ether*	12	62—63° (10)	1.4885	0.9240	46.82	46.42	—	—	$C_{10}H_{14}O$	—	—
Tert-amyl phenyl ether	40	104—105 (28)	1.4910	0.9282	51.04	51.24	80.54, 80.73	9.88, 9.93	$C_{11}H_{16}O$	80.46	9.82
1,1-Dimethylbutyl phenyl ether	34	86—87 (6)	1.4961	0.9302	55.97	55.66	81.40, 81.46	9.99, 10.07	$C_{12}H_{18}O$	80.87	10.18
Tert-amyl m-cresyl ether	30	116—117 (29)	1.4912	0.9191	55.20	55.66	80.88, 80.78	10.21, 10.20	$C_{12}H_{18}O$	80.85	10.17

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* Literature data: $n^{20}D$ 1.4880, d_4^{20} 0.9247 [4]. Due to the agreement between the constants, an analysis was not performed.

SUMMARY

1. α-Chloroisopropyl phenyl, α-chloroisopropyl m-cresyl, α-chloroisopropyl guaiacyl and α-chloroisopropyl cyclohexyl ethers were prepared. Their structure was verified by hydrolysis and by reactions with alcohols, phenols and Grignard reagent.

2. It was shown that these ethers are less stable than the corresponding α-chloroethyl ethers.

3. Tert-butyl phenyl, tert-amyl phenyl, tert-amyl m-cresyl and 1,1-dimethylbutyl phenyl ethers (not described in the literature) were synthesized and characterized.

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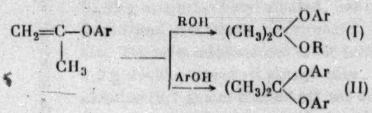
SYNTHESIS AND TRANSFORMATIONS OF α-SUBSTITUTED VINYL ETHERS

VIII. SOME PROPERTIES OF α-METHYLVINYL ARYL AND α-METHYLVINYLCYCLOHEXYL ETHERS

M. F. Shostakovskii, E. P. Gracheva, and N. K. Kul'bovskaia

In the present work we describe the conditions for addition of alcohols and phenols to α-methylvinyl aryl ethers [1] with the objective of preparing alkyl aryl and diaryl ketals (I) and (II); we also consider the polymerization of α-methylvinyl aryl ethers by an ionic mechanism.

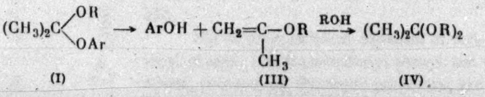


$$CH_2{=}C(CH_3){-}OAr \xrightarrow{ROH} (CH_3)_2C(OAr)(OR) \quad (I)$$

$$CH_2{=}C(CH_3){-}OAr \xrightarrow{ArOH} (CH_3)_2C(OAr)_2 \quad (II)$$

The synthesis of ketals (I, II) is not mentioned in the literature. Methods of preparation of the corresponding acetals are known [2, 3], and their properties have been studied. In particular their susceptibility to disproportionation and to ready cleavage of phenol has been demonstrated. It is interesting to note that ketals are very much more prone to disproportionate and to split off alcohols [4, 5]. This characteristic enables us to obtain α-substituted vinyl ethers starting from 2,2-dimethoxyalkanes [4]. Under similar conditions ethylidene acetals $RCH(OCH_3)_2$ do not give the corresponding unsaturated ethers.

We attempted to realize the synthesis of alkyl aryl ketals in presence of an inorganic acid (HCl) by reacting α-methylvinyl aryl ethers with alcohols. The resulting ketal (I) decomposed, however, into phenol and α-methylvinyl alkyl ether (III); the latter reacts with the alcohol to give a dialkyl ketal (IV) if excess of alcohol is used in the reaction.



$$\underset{(I)}{(CH_3)_2C(OR)(OAr)} \rightarrow ArOH + \underset{(III)}{CH_2{=}C(CH_3){-}OR} \xrightarrow{ROH} \underset{(IV)}{(CH_3)_2C(OR)_2}$$

Alkyl aryl acetals likewise tend to split off phenols [3] when heated, but they can be isolated in the pure form. The tendency of alkyl aryl ketals to split off phenols is so great that mixed ketals cannot be prepared. The behavior of butyl cyclohexyl ketals illustrates the instability of mixed ketals.

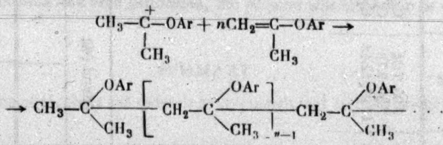
Addition of phenols to α-methylvinyl aryl ethers in presence of mineral acid leads to formation of diaryl ketals (II) which have not been described in the literature. It was not possible, however, to prepare mixed diaryl ketals or symmetrical diguaiacyl and dicyclohexyl ketals.

The susceptibility of α-methylvinyl aryl and α-methylvinyl cyclohexyl ethers to polymerization was investigated. We know that polymerization of ethers by an ionic mechanism proceeds with greater facility at the boiling point of the original ethers [6], and the reaction of high-boiling ethers is effected at reduced pressure. We therefore performed the polymerization of the ethers in question in vacuo at a temperature corresponding to the boiling point of the original ether. Boron fluoride etherate was used as catalyst. Under these conditions a small quantity of viscous polymer is formed. Elementary analysis for C, H and O indicates that polymerization goes with partial decomposition.

When polymerization of these ethers is performed in presence of boron fluoride etherate in the cold (−5°), viscous polymers are obtained whose elemental composition (C, H and O) corresponds to that of the original monomers. The yield of these low-molecular products was extremely low; their molecular weight is more than twice that of the monomer. Characteristics of the prepared polymers are given in Table 2.

We represent the mechanism of polymerization of α-methyl aryl ethers in the first stage of the reaction in presence of ionic catalysts in the following form: $BF_3 + H_2O$ (trace) → $(BF_3 \cdot OH^-) + H^+$.

Subsequently a carbonium ion is formed under the action of the proton:



$$CH_3-\overset{+}{C}(CH_3)-OAr + nCH_2{=}C(CH_3)-OAr \rightarrow$$

$$\rightarrow CH_3-C(OAr)(CH_3)-\left[CH_2-C(OAr)(CH_3)\right]_{n-1}-CH_2-C(OAr)(CH_3)-\ldots$$

EXPERIMENTAL

The starting α-methylvinyl aryl ethers were synthesized by the method developed by us [7].

1. Preparation of diphenyl ketal. 18.4 g α-methylvinyl phenyl ether and 12.9 g phenol were placed in a 100 ml 3-necked flask fitted with stirrer, thermometer and reflux condenser. After 1 drop of 33% hydrochloric acid had been introduced, the temperature rose from 20 to 93°. The mixture was left overnight. The faint-yellow solution was neutralized with anhydrous sodium carbonate, the precipitate was filtered off, and the filtrate was distilled. After a mixture of unreacted ether and phenol had come over, 12.1 g diphenyl ketal was isolated; b. p. 154-155° (12 mm).

Di-m-cresyl ketal and butyl cyclohexyl ketal were prepared by the same procedure. Results are presented in Table 1.

2. Reaction of α-methylvinyl phenyl ether with ethyl alcohol. 20 g α-methylvinyl phenyl ether and 7 g (slight excess) anhydrous alcohol were put into a 100 ml 3-necked flask fitted with mechanical stirrer, thermometer and reflux condenser. The mixture was well stirred, and 1-2 drops of 33% hydrochloric acid was added. The reaction temperature was observed to rise from 20 to 100°. The mixture was left overnight. The yellow solution was neutralized with anhydrous sodium carbonate, the precipitate was filtered off, and the filtrate was distilled to give the following fractions: 1st, b. p. 26-48° (30 mm), 1.9 g; 2nd, b. p. 48-53° (30 mm), 1.3 g; 3rd, b. p. 70-83° (28 mm), 1.1 g; 4th, b. p. 83-105° (26 mm), 12.9 g; 5th, b. p. 110-160° (26 mm), 2 g. The residue was 1.1 g of tarry liquid.

4.9 g of liquid was collected in a trap (after the receiver) which was immersed in a mixture of acetone and dry ice. The 1st and 2nd fractions and the trapped liquid were treated with metallic sodium in diethyl ether. Redistillation gave 1.2 g (10%) of α-methylvinyl ethyl ether with b. p. 62-63° (754 mm), $n^{20}D$ 1.3900*; and 0.8 g diethyl ketal with b. p. 113° (754 mm), $n^{21}D$ 1.3867. 12.8 g phenol was obtained from the 3rd and 4th fractions.

3. Reaction of α-methylvinyl guaiacyl ether with butyl alcohol. The above procedure was employed for reaction of 5 g α-methylvinyl guaiacyl ether with 4.5 g anhydrous butyl alcohol. The following fractions were obtained: 1st, b. p. 52-58° (44 mm), 1.8 g; 2nd, b. p. 75-77° (27 mm), 3.1 g; 3rd, b. p. 105-108° (27 mm), 2.7 g. Treatment with metallic sodium in diethyl ether followed by redistillation of the 1st and 2nd fractions gave 2.5 g (36.5%) of dibutyl ketal with b. p. 94° (35 mm), $n^{20}D$ 1.4170.** The 3rd fraction gave 2.3 g guaiacol.

4. Ionic polymerization of α-methylvinyl aryl and α-methylvinyl cyclohexyl ethers in presence of boron fluoride etherate by boiling in vacuo [6]. A weighed quantity (5-8 g) of the ether was placed in a 3-necked flask

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* According to [8] the compound has b. p. 61-62° (752 mm), $n^{20}D$ 1.3913.

** Literature [1]: b. p. 69-70° (24 mm), $n^{20}D$ 1.4150.

TABLE 1

Physicochemical Constants of Synthesized Ketals

Name of compound	Yield (%)	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D		Found (%)		Empirical formula	Calculated (%)	
					found	calc.	C	H		C	H
Diphenyl ketal	39	154—155° (12)	1.5502	1.0702	67.94	67.55	78.88, 78.81	7.05, 7.04	$C_{15}H_{16}O_2$	78.91	7.06
Di-m-cresyl ketal	20	175—177 (15)	1.5423	1.0342	77.82	76.79	79.55, 79.41	7.59, 7.73	$C_{17}H_{20}O_2$	79.64	7.86
Butyl cyclohexyl ketal	19	113—114 (15)	1.4432	0.8994	63.19	63.32	73.58, 72.61	11.97, 12.13	$C_{13}H_{26}O_2$	72.85	12.23

TABLE 2

Characteristics of Polymers of α-Methylvinyl Aryl Ethers

Name of ether	Experimental conditions	Appearance	Yield (%)	Molecular weight*	Viscosity (in centipoises)	Found (%)		Empirical formula	Calculated (%)	
						C	H		C	H
α-Methylvinyl phenyl	Boiling in vacuo, 1 hr	Light-yellow, viscous	36	299.4, 295.1	0.6890	82.40, 82.17	6.75, 6.95	$C_9H_{10}O$	80.6	7.52
α-Methylvinyl phenyl	Cooling at −5°, 4 hrs	Light-yellow, viscous	57	278.3, 285.4	0.6810	80.71, 80.58	7.47, 7.64	$C_9H_{10}O$	80.6	7.52
α-Methylvinyl m-cresyl	Boiling in vacuo, 1 hr	Light-brown, viscous	38	338.4, 348.7	0.6798	83.24, 83.41	8.91, 8.78	$C_{10}H_{12}O$	81.16	8.14
α-Methylvinyl guaiacyl	Boiling in vacuo, 1 hr	Light-brown, solid	26	376.1, 360.0	0.6916	78.17, 78.04	8.30, 8.21	$C_{10}H_{12}O$	73.25	7.35
α-Methylvinyl guaiacyl	Cooling to −5°, 4 hrs	Light-yellow, viscous	51	350.2, 342.8	0.6811	73.49, 73.35	7.48, 7.46	$C_{10}H_{12}O_2$	73.25	7.35
α-Methylvinyl cyclohexyl	Boiling in vacuo, 1 hr	Light-yellow, viscous	40	298.1, 312.0	0.6847	79.47, 79.50	10.80, 10.68	$C_9H_{16}O$	77.80	11.50

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* Cryoscopically in benzene.

fitted with reflux condenser attached to a Vigreux column, a thermometer, and a capillary extending to the bottom of the flask. The ether was heated on an oil bath to boiling point in the vacuum of a water jet pump. Addition of 2-3 drops of a freshly prepared 12% solution of BF_3 etherate in diethyl ether caused a slight rise (10-25°) of temperature and darkening of the solution. After 30 min heating, the flask was cooled, and a stream of gaseous ammonia was introduced to neutralize the catalyst. The viscous solution was transferred to a flask for steam distillation. After 150 ml water had distilled over, a reddish resin was observed in the residue. The resin was separated from water and dissolved in benzene, and the benzene was driven off at 40-50 mm. The residue was brought to constant weight in a vacuum-desiccator. Results are presented in Table 2.

5. Ionic polymerization of α-methylvinyl aryl ethers in presence of boron fluoride etherate at low temperature. A weighed amount of ether (5-10 g) was placed in a 3-necked flask fitted with stirrer and thermometer. The flask was cooled to −5°. The temperature of the mass rose to +5° when a drop of 12% solution of BF_3 etherate in diethyl ether was added. The mixture was kept at this temperature for 3-4 hrs, after which it was brought to room temperature. After gaseous ammonia had been introduced, the polymer was worked up as described above. Results are presented in Table 2.

SUMMARY

1. Conditions for addition of alcohols and phenols to α-methylvinyl aryl and α-methylvinyl cyclohexyl ethers were investigated.

2. It was shown that alkyl aryl ketals are incapable of existence and easily break down with liberation of phenol.

3. The possibility of indirect preparation of α-methylvinyl alkyl ethers was demonstrated, starting from α-methylvinyl aryl ether and the appropriate alcohol (via ketals).

4. Diphenyl and di-m-cresyl ketals and butyl cyclohexyl ketal (not previously described in the literature) were prepared.

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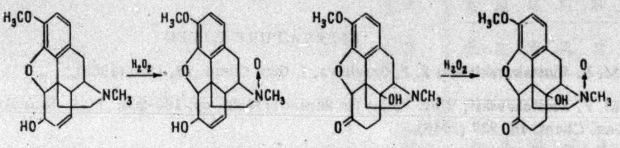
SYNTHESIS AND STUDY OF N-OXIDES OF HETEROCYCLIC COMPOUNDS

I. N-OXIDE DERIVATIVES OF MORPHINE, TETRAHYDROISOQUINOLINE AND QUINOLINE

A. M. Khaletskii, V. G. Pesin, and Chou Ts'in

Heterocyclic N-oxides have been known for a long time, but their chemistry has been inadequate studied; certain N-oxides are interesting not only biologically (iodinin, aspergillic acid, etc.) but they also possess value in the synthesis of difficultly available compounds (4-nitropyridine, etc. [1]). In this communication we present the data obtained in a study of the synthesis and properties of some N-oxide derivatives of morphine, tetrahydroisoquinoline and quinoline.

The oxidation of codeine (I) with 3% hydrogen peroxide gave codeine N-oxide (II), m. p. 206-208° (literature [2], m. p. 230-231°); the oxidation of dihydrohydroxycodeinone (III) with 3% H_2O_2 in alcohol medium gave the corresponding N-oxide (IV), m. p. 152-153° (with decomp.), whose picrate had m. p. 190-192°, and whose hydrochloride had m. p. 167-168°.



(I) (II) (III) (IV)

Dihydrohydroxycodeinone N-oxide (IV) reacts in a peculiar manner with sulfur dioxide; reaction of the latter with an alcoholic solution of (IV) yields a water-soluble substance (VI), m. p. 169-170°; an aqueous solution of (VI) when made alkaline with sodium hydroxide gave the original dihydrohydroxycodeinone (III) as a precipitate. Acidification of an aqueous solution of (VI), followed by the addition of barium chloride, gave a precipitate of barium sulfate. From this it could be postulated that dihydrohydroxycodeinone N-oxide (IV) reacts with sulfurous acid* to form the sulfate of dihydrohydroxycodeinone (III).

$$(IV) \xrightarrow{H_2SO_3} (III) - \begin{cases} \xrightarrow{KOH} (III) \\ \xrightarrow{HCl+BaCl_2} (III) + BaSO_4 \end{cases}$$

However, such a postulation is not supported experimentally. Substance (VI) melts at 169-70°, whereas the sulfate of (III) melts at 138-139°; the mixed melting point of the latter with (VI) shows a depression. In addition, based on the analysis data, the composition of substance (VI) corresponds to that of the hydrate. On the basis of the presented data it is possible to postulate that the oxidation of dihydrohydroxycodeinone (III) yields the corresponding N-oxide hydrate (V), which when reacted with sulfur dioxide is converted to a compound that is isomeric with the sulfate (VI).

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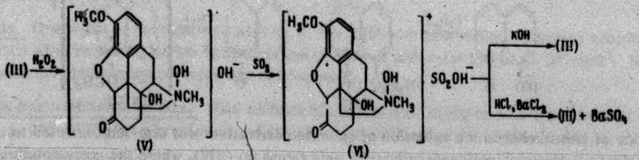
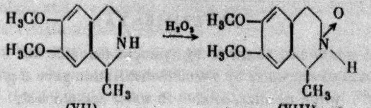
* Although the reaction was run with dry sulfur dioxide gas in anhydrous alcohol, still it could always be assumed that a trace amount of moisture (0.026 g), necessary to form sulfurous acid [based on the amount of (III) consumed], is present under the experimental conditions.



Consequently, the oxidation of (III) yields a completely substituted ammonium derivative of the type $[(R)_3NOH]^+OH^-$, where R, a hydrocarbon radical, is converted on further treatment with sulfur dioxide to sulfate (VI), by analogy with the example cited in [3].

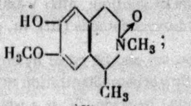
$$[(R)_3NOH]^+OH^- + HCl \rightarrow [(R)_3NOH]^+Cl^- + H_2O$$

The oxidation of salsolidine (VII) with 3% hydrogen peroxide in aqueous acetone gave substance (VIII), m. p. 100-101°, which reduced Fehling solution and ammoniacal silver oxide solution, but which failed to give any derivatives characteristic for the aldehyde group. It is possible to assume that the substance is N-hydroxysalsolidine, having the structure of (VIII).

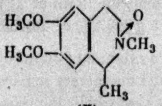


(VII) (VIII)

When salsoline was oxidized with either hydrogen peroxide or perbenzoic acid we were unable to isolate N-hydroxysalsolidine, which is in agreement with the literature data [4] on the lesser activity of salsoline when compared with salsolidine. The oxidation of the N-methyl derivatives of salsolidine and salsoline led to the quite easy formation of the corresponding N-oxides (IX and X).



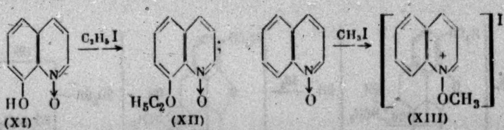
(IX)



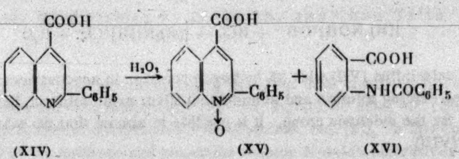
(X)

As regards the N-oxides of the 8-hydroxy- and 8-ethoxyquinolines, then judging by the literature data [5], it is possible to obtain them by the oxidation of the original quinolines with perbenzoic acid; the oxidation of 8-hydroxyquinoline with hydrogen peroxide in the presence of glacial acetic acid enabled us to obtain the corresponding N-oxide in very low yield, while the oxidation of 8-ethoxyquinoline under the indicated conditions failed to give us even traces of 8-ethoxyquinoline N-oxide. Positive results were obtained only when the 8-hydroxy- and 8-ethoxyquinolines were heated with hydrogen peroxide to 50-60° in the presence of acetic acid. As was established by us, 8-hydroxyquinoline N-oxide is formed in much smaller yield than is 8-ethoxyquinoline N-oxide, which can be explained by the influence of the hydrogen bond in the structure of 8-hydroxyquinoline. In view of the fact that 8-ethoxyquinoline N-oxide melts at 60° and even considerably lower when impure, we purified it through the picrate and the hydrochloride; the free base was isolated from the hydrochloride.

The ethylation of 8-hydroxyquinoline N-oxide with ethyl iodide gave 8-ethoxyquinoline N-oxide (XII) in 62% yield; in this respect 8-hydroxyquinoline N-oxide differs sharply from quinoline N-oxide [as is known, the methylation of the latter yields the iodide with structure (XIII)].



The influence of substituents on the oxidation of quinoline derivatives was also demonstrated to us in the action of peracetic acid on 2-phenylquinoline-4-carboxylic acid (atophan) (XIV), where the corresponding N-oxide (XV) was isolated in 80% yield; when the oxidation was run with an excess of 30% hydrogen peroxide in the presence of aqueous acetic acid we isolated, besides atophan N-oxide (XV), also N-benzoylanthranilic acid (XVI).



EXPERIMENTAL

Codeine N-oxide (II). A mixture of 45 ml of 3% hydrogen peroxide and 8.4 g of codeine (I) was heated on a water bath at 50-60°; removal of the water by vacuum-distillation gave 8 g of (II), which after recrystallization from water melted at 206-208°; white needles, soluble in water and alcohol.

Found %: N 4.37, 4.51. $C_{18}H_{21}O_4N$. Calculated %: N 4.44.

Codeine N-oxide hydrochloride. A hot solution of 1.6 g of (II) in 5 ml of alcohol, obtained by heating on the water bath, was treated with 1 ml of hydrochloric acid (d 1.19); we obtained 1.35 g (87%) of substance with m. p. 209-214°. After recrystallization from alcohol, m. p. 214-217°.

Dihydrohydroxycodeinone N-oxide (tecodine) (IV). A solution of 5 g of dihydrohydroxycodeinone hydrochloride in 40 ml of water was treated with 10 ml of 10% NaOH solution; after washing the precipitate with water and drying at 100° we obtained 4.15 g (93.2%) of dihydrohydroxycodeinone (III), m. p. 213-216°.

7 g of (III) was added to a mixture of 40 ml of alcohol and 30 ml of hydrogen peroxide (3%); the mixture was heated on the water bath and the solvent removed by vacuum-distillation to give 3.25 g (46.2%) of substance, m. p. 152-153° (with decomp.). Dihydrohydroxycodeinone N-oxide (IV) is a white crystalline powder, difficultly soluble in alcohol, and moderately soluble in water; it forms a red color when heated with acetic anhydride.

Found %: C 62.18, 61.51; H 6.66, 6.76; N 3.97, 3.71. $C_{18}H_{23}O_6N$. Calculated %: C 61.89; H 6.59; N 4.01.

Dihydrohydrocodeinone N-oxide picrate. The picrate was obtained by adding a saturated solution of picric acid to an alcohol solution of dihydrohydroxycodeinone N-oxide; the precipitate after drying had m. p. 190-192.

Dihydrohydroxycodeinone N-oxide hydrochloride. An alcohol solution of HCl was added to an alcohol solution of 0.8 g of dihydrohydroxycodeinone N-oxide; the solution was concentrated in vacuo, and after standing for 10 days, gave 0.65 g of substance, which after recrystallization from alcohol, and then from ether, melted at 167-168°. The compound was obtained as white needles, readily soluble in alcohol and in water.

Isomer of dihydrohydroxycodeinone sulfate (VI ?). Dihydrohydroxycodeinone N-oxide (IV) (0.5 g) was dissolved in anhydrous alcohol with heating, and the solution was saturated with dry sulfur dioxide, obtained by the decomposition of sodium sulfite with sulfuric acid. Evaporation of the alcohol solution gave 0.37 g (62.5%) of substance, which after recrystallization from anhydrous alcohol melted at 169-170° (with decomp.). The compound is readily soluble in water and gives a precipitate of barium sulfate when treated with barium chloride in the presence of hydrochloric acid.

Found %: C 52.23, 52.12; H 5.72, 5.58; N 3.16, 3.22; S 7.85, 7.59. $C_{18}H_{23}O_8NS$. Calculated %: C 52.23; H 5.57; N 3.16, 3.22; S 7.75.

Hydrolysis. Hydrolysis of the substance with m. p. 169-170° with 10% sodium hydroxide solution gave a precipitate, which after recrystallization from a mixture of alcohol and water had m. p. 207-209°; the mixed melting point with dihydrohydroxycodeinone was not depressed.

Dihydrohydroxycodeinone sulfate. The addition of concentrated H_2SO_4 to an alcohol solution of the substance with m. p. 207-209° gave a precipitate, which after recrystallization from water had m. p. 138-139°.

N-Hydroxysalsolidine (VIII). A mixture of 3 g of salsolidine (VII), 20 ml of acetone and 30 ml of water was treated with 2.5 ml of 30% hydrogen peroxide. The mixture was allowed to stand at room temperature for several days, after which the acetone was distilled off, and the aqueous solution was extracted with ether. The ether solution after drying over anhydrous sodium sulfate was distilled to remove the ether; we obtained 0.5 g (15.48%) of substance, which after recrystallization from a mixture of alcohol and water had m. p. 100-101°. The compound was obtained as a white powder, and reduced both Fehling solution and ammoniacal silver oxide solution.

Found %: C 64.65, 64.67; H 7.34, 7.44; N 6.33, 6.39. $C_{12}H_{17}O_3N$. Calculated %: C 64.57; H 7.62; N 6.28.

1,2-Dimethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline N-oxide* (N-methylsalsolidine N-oxide) (IX). A mixture of 6 g of N-methylsalsolidine, 25 ml of 95% alcohol, 25 ml of water and 3.5 ml of 30% hydrogen peroxide solution was stirred for 4 days, after which the aqueous alcohol solution was vacuum-distilled, the residual yellowish liquid dissolved in alcohol, and the alcohol solution treated with a saturated alcohol solution of picric acid. We obtained 11 g of N-methylsalsolidine N-oxide, m. p. 122-130°; after recrystallization from a mixture of alcohol and water (1 : 1), m. p. 133-134°. Reaction of the picrate of N-methylsalsolidine N-oxide with hydrochloric acid gave the hydrochloride, which was extracted with hot benzene after removal of the picric acid by filtration. The hydrochloride of N-methylsalsolidine N-oxide after purification with alcohol and ether had m. p. 162-163° (with decomp.).

Found %: C 57.32, 57.51; H 7.41, 7.57; N 5.32, 5.28. $C_{13}H_{19}O_3N \cdot HCl$. Calculated %: C 57.04; H 7.31; N 5.12.

Attempted oxidation of salsoline. a) Oxidation with hydrogen peroxide. A solution of 1 g of salsoline in 8 ml of 98% acetic acid was treated with 10 ml of 3% hydrogen peroxide; the mixture was heated on the water bath, the water was vacuum-distilled, and the residue, a thick red oily liquid, was treated with alcohol and 1 ml of hydrochloric acid. The obtained precipitate had m. p. 212° and did not give a melting point depression when mixed with authentic salsoline.

b) Oxidation with hydrogen peroxide in neutral medium. A mixture of 1 g of salsoline and 100 ml of 95% alcohol was heated on the water bath at 60°. The mixture on cooling gave a crystalline substance with m. p. 210°, which did not depress the melting point when mixed with authentic salsoline.

c) Oxidation with perbenzoic acid. A mixture of 1 g of salsoline, 80 ml of chloroform and 10 ml of alcohol was heated under reflux, and then with ice cooling the solution was treated with 70 ml of a chloroform solution containing 1.2 g of perbenzoic acid. An individual substance could not be isolated when the yellowish-brown residue was treated with 10% ammonia solution.

N-Methylsalsoline N-oxide (X). A mixture of 0.5 g of N-methylsalsoline,** 10 ml of water and 0.3 ml of 30% hydrogen peroxide was stirred for 3 days, after which the reaction mixture was vacuum-distilled at a temperature not exceeding 40°. Treatment of the residual viscous liquid with an alcohol solution of hydrogen chloride gave 0.3 g of a white precipitate with m. p. 172-174°, which after recrystallization from alcohol and ether had m. p. 186°, and was readily soluble in water. Treatment with 25% ammonia solution gave white crystals with m. p. 181-183° (with decomp.).

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* 1,2-Dimethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline was obtained by the method described in the literature [6]; its picrate had m. p. 218.

** 1,2-Dimethyl-6-hydroxy-7-methoxytetrahydroisoquinoline with m. p. 139-142° was obtained by the method described in the literature [7].

Found %: C 55.21, 55.30; H 7.20, 7.04; N 5.47, 5.38. $C_{12}H_{17}O_3N \cdot HCl$. Calculated %: C 55.50; H 6.93; N 5.39.

8-Hydroxyquinoline N-oxide (XI). a) Oxidation of 8-hydroxyquinoline with perbenzoic acid. A chloroform solution of perbenzoic acid, containing 0.512 g of active oxygen, was cooled to 1° and then 4.5 g of 8-hydroxyquinoline in 20 ml of chloroform was added gradually. The next day the chloroform was vacuum-distilled, and the viscous residue was first washed with ammonia solution by decantation, then with water, and finally recrystallized from water. The compound was obtained as yellow needles with m. p. 137-138°.

b) Oxidation of 8-hydroxyquinoline with peracetic acid. A mixture of 25 ml of 98% acetic acid, 19.2 ml of acetic anhydride and 25 ml of 30% hydrogen peroxide was heated at 40-45°, and in 3 hrs 5 g of 8-hydroxyquinoline was added gradually with constant stirring. A large amount of heat was evolved during reaction, the temperature of the solution rose to 100°, and the solution turned red. The solution was cooled to 50°, kept at this temperature for 16 hrs, the acetic acid vacuum-distilled from the reaction mixture, the residue treated with water, and the precipitate filtered. The aqueous solution was extracted 3 times with chloroform, and the chloroform solution was washed with water, dried over calcium chloride, and then evaporated on the water bath to dryness. We obtained 1.1 g (20%) of yellow needle crystals, which after recrystallization from water had m. p. 133-134°. The mixed melting point with 8-hydroxyquinoline N-oxide was not depressed.

c) Oxidation of 8-hydroxyquinoline with hydrogen peroxide. A solution of 10 g of 8-hydroxyquinoline in 50 ml of 98% acetic acid was treated with 22 ml of 30% hydrogen peroxide solution, and then the mixture was heated to the boil. After 2 hrs the solution was neutralized with ammonia solution, and the obtained precipitate was recrystallized from a mixture of alcohol and water; m. p. 74-75°. The mixed melting point with 8-hydroxyquinoline was not depressed.

8-Ethoxyquinoline N-oxide (XII). a) A mixture of 0.8 g of 8-hydroxyquinoline N-oxide and 0.3 g of potassium hydroxide was dissolved in 30 ml of alcohol, and then 1 ml of ethyl iodide was added to the solution with constant stirring. The mixture was then heated on the water bath for 1 hr at the boil, the alcohol distilled off, and the residue treated with 10% sodium hydroxide solution. The alkaline solution was extracted with ether, and the ether solution was washed with water, then dried over anhydrous sodium sulfate, and finally evaporated to dryness. The residual brownish oil was treated with alcohol, and then an alcohol solution of picric acid was added; removal of the alcohol gave the picrate, which after recrystallization from alcohol had m. p. 135-138°. The mixed melting point with the picrate of 8-ethoxyquinoline N-oxide, the latter obtained by the oxidation of 8-ethoxyquinoline with peracetic acid, was not depressed.

b) A mixture of 150 ml of 98% acetic acid, 120 ml of acetic anhydride and 138 ml of 30% hydrogen peroxide was heated with constant stirring for 3 hrs at 45-50° in a flask fitted with a reflux condenser and dropping funnel; then 30 g of 8-ethoxyquinoline, obtained by the method described in the literature [8], was added gradually (here a temperature rise to 85° was observed). Then the mixture was stirred for 16 hrs at 50°. After this most of the liquid was vacuum-distilled, 200 ml of water was added to the residue, the removal of the liquid by vacuum-distillation repeated, the residue diluted with water, the solution neutralized with 10% sodium hydroxide solution, and the resulting viscous brown oil extracted with chloroform. The chloroform solution was washed with water, dried over calcium chloride, and then stirred with 36 g of picric acid to give 49.4 g (60.77%) of 8-ethoxyquinoline N-oxide picrate. After recrystallization from ethyl alcohol, m. p. 137-138°.

8-Ethoxyquinoline N-oxide hydrochloride. 8-Ethoxyquinoline N-oxide picrate (18 g) was mixed with 45 ml of hydrochloric acid (d 1.19), and the obtained picric acid was filtered. The filtrate was extracted with hot benzene (to remove picric acid), then evaporated in vacuo at 30-40° to an oily liquid, and the latter treated with alcohol and ether. The obtained yellow needle crystals were filtered and dried in a desiccator; we obtained 3.68 g (38%) of 8-ethoxyquinoline N-oxide hydrochloride, m. p. 158°.

8-Ethoxyquinoline N-oxide. A solution of 0.97 g of 8-ethoxyquinoline N-oxide hydrochloride in 1.5 ml was treated with 4 ml of 10% sodium hydroxide solution. Since the free base failed to separate here, the solution was extracted with chloroform and after drying over calcium chloride the chloroform solution was evaporated; we obtained 0.8 g (98%) of white needle crystals with m. p. 56-58°. After recrystallization from ether, m. p. 61-62°.

Found %: C 69.34, 69.67; H 5.69, 5.76; N 7.37, 7.55. $C_{11}H_{11}O_2N$. Calculated %: C 69.84; H 5.82; N 7.40.

2-Phenylquinoline-4-carboxylic acid N-oxide (XV). A mixture of 250 ml of 98% acetic acid and 120 ml of 30% hydrogen peroxide, after heating on the boiling water bath, was treated with 20 g of 2-phenylquinoline-4-carboxylic acid (XIV), added portionwise in 1 hr and with stirring. Heating the mixture for 5 hrs on the boiling water bath gave a yellow precipitate, which after recrystallization from alcohol had m. p. 244°; yield 15.91 g (76%). The compound is readily soluble in ethyl and methyl alcohol, in chloroform, and is insoluble in water.

Found %: C 72.55, 72.27; H 4.20, 4.45; N 5.21, 5.20. $C_{16}H_{11}O_3N$. Calculated %: C 72.44; H 4.18; N 5.28.

N-Benzoylanthranilic acid (XVI). Recrystallization of the second portion of precipitate (obtained on pouring the acetic acid solution into water) gave N-benzoylanthranilic acid, which was obtained as pale yellow crystals with m. p. 170-172°; the yield was 3 g (15.78%, based on 2-phenyl-4-carboxylic acid).

Found %: C 69.51, 69.91; H 4.72, 4.74. $C_{14}H_{11}O_3N$. Calculated %: C 69.71; H 4.57.

Oxidation of 2-phenylquinoline-4-carboxylic acid with perbenzoic acid. A suspension of 1 g of atophan in 100 ml of chloroform was treated with 22 ml of a chloroform solution containing 0.84 g of perbenzoic acid. After 2 days the insoluble portion was filtered and recrystallized from alcohol, m. p. 210°. The mixed melting point with atophan was not depressed.

Oxidation of 2-phenylquinoline-4-carboxylic acid with hydrogen peroxide. 1 g of atophan in a mixture (1:1) of acetone and alcohol (75 ml) was oxidized with 8 ml of a 25% hydrogen peroxide solution at 50°. After removal of the solvents by vacuum-distillation the isolated precipitate had m. p. 206-208°, and failed to depress the melting point when mixed with atophan.

Reduction of 2-phenylquinoline-4-carboxylic acid N-oxide. A mixture of 0.5 g of atophan N-oxide, 1.5 g of sodium hydrosulfite, 10 ml of alcohol and 10 ml of water was heated under reflux for 3 hrs. The crystalline powder obtained on cooling was dried at 90°; we obtained 0.2 g of substance with m. p. 205-207°. The mixed melting point with atophan was not depressed.

SUMMARY

1. The reaction of H_2O_2 with codeine, dihydrohydroxycodeinone, salsolidine, N-methylsalsolidine N-oxide, salsoline, N-methylsalsoline N-oxide, 8-hydroxyquinoline, 8-ethoxyquinoline and 2-phenylquinoline-4-carboxylic acid was studied, in which connection the corresponding N-oxides were isolated.

2. It was found that the reaction of dihydrohydroxycodeinone with sulfur dioxide yields a substance with m. p. 169-170° (with decomp.), which when hydrolyzed in the presence of caustic is converted to dihydrohydroxycodeinone. It was also found that the substance with m. p. 169-170° is different from the sulfate of dihydrohydroxycodeinone with m. p. 138-139°.

3. The reaction of peracetic acid with 8-hydroxyquinoline was investigated, and the N-oxide of the latter with m. p. 133-134° was isolated.

4. The reaction of perbenzoic acid with salsoline, 8-hydroxyquinoline and 2-phenylquinoline-4-carboxylic acid was investigated, in which connection only the N-oxide of 8-hydroxyquinoline was isolated.

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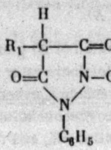
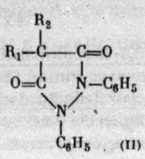
CHEMISTRY OF PYRAZOLIDINE

I. SYNTHESIS AND STUDY OF SOME MONO- AND DISUBSTITUTED DERIVATIVES OF 1,2-DIPHENYL-3,5-DIOXOPYRAZOLIDINE

A. M. Khaletskii, V. G. Pesin, and Têng Jun-Hsiang

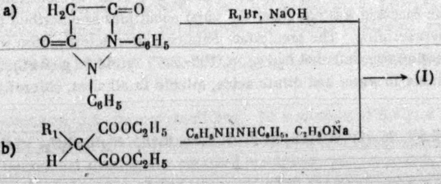
Despite the fact that pyrazolidine has been known for a long time, the chemistry of its derivatives has received inadequate study; this is especially pertinent to compounds of the type of (I) and (II).

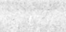
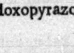
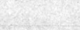

(I)


(II)

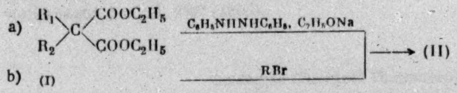
R_1 and R_2 are various radicals.

Derivatives of the (I) type can be obtained by various methods [1, 2]. We investigated the following reactions: a) reaction of 1,2-diphenyl-3,5-dioxopyrazolidine with alkyl halides, and b) reaction of an alkylmalonic ester with hydrazobenzene.



Based on the patent data [3], reaction "a" is run by reacting the starting substances at 70° in the presence of 2 N sodium hydroxide solution. When this reaction was studied by us it was found that it is impossible to isolate any noticeable amount of 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine under the indicated conditions; negative results were also obtained when the water was replaced by anhydrous alcohol. Satisfactory results were obtained when reaction "b" was studied, and here the mentioned product was isolated in 60% yield. The same method was used by us to synthesize other type (I) compounds, where R = n-C_4H_9, C_6H_5,  —, CH_3OCH_2, $C_2H_5OCH_2$, $(CH_3)_2NCH_2-CH_2$, $(C_2H_5)_2N-CH_2-CH_2$. The synthesis of derivatives of the (II) type, where R_1R_2 = = CH_3, n-C_4H_9; C_2H_5, n-C_4H_9; CH_3,  ; C_2H_5,  ; was accomplished by us both by the reaction of disubstituted derivatives of malonic ester with hydrazobenzene in the presence of sodium alcoholate,

and by the reaction of 4-alkyl-1,2-diphenyl-3,5-dioxopyrazolidine with alkyl halides.



Here it was found that reaction "a" proceeds with the greater difficulty. Thus, when either Δ^2-cyclohexenylmethylmalonic ester or Δ^2-cyclohexenylethylmalonic ester is reacted with hydrazobenzene in the presence of sodium alcoholate the corresponding 1,2-diphenyl-3,5-dioxopyrazolidine derivatives are formed in yields of only 2-3%. Consequently, this method does not have practical value, although the indicated reaction does have definite theoretical interest.

It is known that symmetrical disubstituted hydrazines, for example, hydrazobenzene, readily react with malonic ester but show much more difficult reaction with monosubstituted derivatives of malonic ester [2]. As regards the disubstituted derivatives, then based on literature data [4], these compounds are incapable of reacting with symmetrical disubstituted hydrazines to yield derivatives of the (II) type. As was shown by us, the alkylation of the monosubstituted derivatives of 1,2-diphenyl-3,5-dioxopyrazolidine possesses practical value (method "b"). With this method we were able to obtain the 4,4-n-butylmethyl- and 4,4-n-butylethyl-1,2-diphenyl-3,5-dioxopyrazolidines in 80-90% yield.

EXPERIMENTAL

4-n-Butyl-1,2-diphenyl-3,5-dioxopyrazolidine. To a solution of 30 g of sodium metal in 1 liter of anhydrous alcohol was added, with constant stirring, 250 g of n-butylmalonic ester and 212.2 g of hydrazobenzene. The reaction was run in a 3-necked flask, fitted with a reflux condenser protected by a calcium chloride tube, and a thermometer. After boiling on the water bath until a homogeneous solution was obtained, the reflux condenser was replaced by a descending condenser, the alcohol distilled off, and the residue heated with constant stirring for 12 hrs at 130-150°. The solid mass obtained on cooling was treated with 1 liter of water, and the alkaline filtrate was extracted with ether to remove impurities, after which it was acidified until acid to Congo; the obtained yellowish oily precipitate crystallized. Recrystallization from alcohol gave 213 g of substance with m. p. 105° (60%, based on the n-butylmalonic ester), corresponding to the known 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine [3].

4-Δ^2-Cyclohexenyl-1,2-diphenyl-3,5-dioxopyrazolidine. To a solution of 2.07 g of sodium metal in 45 ml of anhydrous alcohol was added with constant stirring 20 g of Δ^2-cyclohexenylmalonic ester and 15.4 g of hydrazobenzene. The reaction was run under the same conditions as described for the synthesis of 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine. The precipitate obtained after acidification with hydrochloric acid was isolated, and after recrystallization from alcohol had m. p. 195-196°; yield 18 g (64%). The compound was obtained as yellow needles, insoluble in water and dilute acids, soluble in alkalies, chloroform and alcohol, and slightly soluble in ether.

Found %: C 75.97, 76.02; H 6.12, 6.17; N 8.53, 8.76. $C_{21}H_{20}O_2N_2$. Calculated %: C 75.90; H 6.02; N 8.44.

4-Dimethylaminoethyl-1,2-diphenyl-3,5-dioxopyrazolidine. To 1.25 g of sodium metal in 30 ml of anhydrous alcohol, contained in a 3-necked flask fitted with a dropping funnel and a reflux condenser protected by a calcium chloride tube, was added with constant stirring 11.5 g of ethyl dimethylaminoethylmalonate and 9.16 g of hydrazobenzene. After heating in an oil bath at 120-130°, followed by distillation of the alcohol, the residue was heated for 10 hrs at 150-160°; the reaction mass after cooling was dissolved in 200 ml of water, the solution filtered, and the filtrate neutralized with dilute hydrochloric acid. The precipitate was washed with ether and then recrystallized from alcohol to give 8 g of substance (49%) with m. p. 235-236° (with decomp.).

Found %: C 70.93, 70.69; H 7.02, 7.67; N 12.88, 12.78. $C_{19}H_{21}O_2N_3$. Calculated %: C 70.59; H 6.50; N 13.00.

The crystalline compound is insoluble in water and ether, and is soluble in dilute acids, alkalies, alcohol and chloroform.

4-Diethylaminoethyl-1,2-diphenyl-3,5-dioxopyrazolidine. The compound was obtained in the same manner as the preceding from 25 g of diethylaminoethylmalonic ester and 14 g of hydrazobenzene in the presence of 2 g of sodium metal and 50 ml of anhydrous alcohol. Yield 15.64 g (46%), m. p. 216-217°. The compound was obtained as white or slightly yellowish crystals, insoluble in water and ether, and soluble in alkalies, acids, chloroform and alcohol.

Found %: C 72.06, 72.04; H 7.53, 7.34; N 12.38, 11.97. $C_{21}H_{25}O_2N_3$. Calculated %: C 71.76; H 7.17; N 11.97.

4-Methoxymethyl-1,2-diphenyl-3,5-dioxopyrazolidine. Obtained in the same manner as the preceding from 10.2 g of methoxymethylmalonic ester and 9.2 g of hydrazobenzene in the presence of 1.4 g of sodium metal in 40 ml of alcohol. Yield 7.4 g (50%), m. p. 80-88° (with decomp.). The compound was obtained as an amorphous brownish substance, soluble in alkalies, alcohol, benzene, chloroform and ether, and insoluble in water and acids.

Found %: C 68.53, 68.41; H 5.27, 5.40; N 9.46, 9.37. $C_{17}H_{16}O_3N_2$. Calculated %: C 68.92; H 5.44; N 9.46.

4-Ethoxymethyl-1,2-diphenyl-3,5-dioxopyrazolidine. Obtained in the same manner as the preceding from 10.9 g of ethoxymethylmalonic ester, b. p. 115-120° (10 mm), and 9.2 g of hydrazobenzene in the presence of 1.4 g of sodium metal in 40 ml of anhydrous alcohol. Yield 7.8 g (50%), m. p. 55-60° (with decomp.). The compound was obtained as an amorphous substance with properties close to those of the 4-methoxy analog.

Found %: C 69.42, 69.85; H 5.62, 5.62; N 9.50, 9.75. $C_{18}H_{18}O_3N_2$. Calculated %: C 69.68; H 5.81; N 9.03.

4-Methyl-4-Δ^2-cyclohexenyl-1,2-diphenyl-3,5-dioxopyrazolidine. To a solution of 3.22 g of sodium metal in 60 ml of anhydrous alcohol was added with constant stirring 32.2 g of methyl-Δ^2-cyclohexenylmalonic ester and 23.18 g of hydrazobenzene. The reaction was run under the conditions described for the synthesis of 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine. Yield 1.1 g (3%), m. p. 134-136°. The compound was obtained as white crystals, insoluble in water, acids and alkalies, and soluble in ether, alcohol and chloroform.

Found %: C 76.67, 76.87; H 6.33, 6.30; N 9.34, 9.18. $C_{22}H_{22}O_2N_2$. Calculated %: C 76.30; H 6.36; N 8.09.

4-Ethyl-4-Δ^2-cyclohexenyl-1,2-diphenyl-3,5-dioxopyrazolidine. Obtained in the same manner as the preceding from 30 g of ethyl-Δ^2-cyclohexenylmalonic ester and 21.15 g of hydrazobenzene in the presence of 3.45 g of sodium metal and 150 ml of anhydrous alcohol. Yield 1.2 g (3%), m. p. 140-141°. The compound was obtained as white crystals, insoluble in water, acids and alkalies, and soluble in alcohol, ether and chloroform.

Found %: C 76.94, 76.72; H 6.91, 6.78; N 8.01, 7.77. $C_{23}H_{24}O_2N_2$. Calculated %: C 76.67; H 6.67; N 7.78.

4-Methyl-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine. To a solution of 8.8 g of 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine in 200 ml of a 1% alcoholic potassium hydroxide solution was added 9 g of methyl iodide. After long standing at 20° with occasional shaking the obtained precipitate was separated, and the solution was concentrated in vacuo to remove alcohol. After adding water and ether the ether layer was separated, washed with 10% sodium hydroxide solution to remove unreacted 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine, and then with water. The ether solution was dried over anhydrous sodium sulfate, the ether removed by evaporation, and the residue recrystallized from alcohol to give 7.8 g (85%) of substance with m. p. 110-111°. The compound was obtained as white crystals, insoluble in alkalies, acids and water, and soluble in alcohol, ether and chloroform.

Found %: C 74.76, 74.46; H 6.03, 6.05; N 8.78, 8.79. $C_{20}H_{22}O_2N_2$. Calculated %: C 74.53; H 6.84; N 8.68.

4-Ethyl-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine. A solution of 8.8 g of 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine in 200 ml of a 1% alcoholic potassium hydroxide solution was treated with 10 g of ethyl iodide, and then the reaction mixture was worked up in the same manner as the preceding; we obtained 8.2 g (87%) of substance with m. p. 72-73°. The compound was obtained as yellowish crystals, insoluble in water, alkalies and acids, and soluble in alcohol, ether and chloroform.

Found %: C 75.35, 75.00; H 7.49, 7.14; N 8.35, 8.72. $C_{21}H_{24}O_2N_2$. Calculated %: C 75.00; H 7.14; N 8.33.

SUMMARY

1. The reaction of monoalkylmalonic esters with hydrazobenzene was studied, in which connection it was found that satifactory yields (< 50%) are obtained if the condensation is run in the presence of sodium metal in anhydrous alcohol medium; this procedure was used to synthesize the following compounds: 4-n-butyl-, 4-Δ^2-cyclohexenyl-, 4-dimethylaminoethyl-, 4-diethylaminoethyl-, 4-methoxymethyl- and 4-ethoxymethyl-1,2-diphenyl-3,5-dioxopyrazolidine. At the same time it was found, contrary to the patent data, that 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine is not formed in any substantial amount when the condensation of hydrazobenzene with n-butylmalonic ester is run in the presence of 2 N sodium hydroxide solution; it is also not formed when the condensation is run in the presence of sodium hydroxide in anhydrous alcohol medium.

2. The reaction of dialkylmalonic esters with hydrazobenzene in the presence of sodium alcoholate was studied, in which connection it was shown, contrary to the literature data, that it is impossible to form dialkyl derivatives of 3,5-dioxopyrazolidine using this method. However, we did synthesize, although in small yields (~ 3%), the 4-Δ^2-cyclohexenyl-4-methyl- and 4-Δ^2-cyclohexenyl-4-ethyl-3,5-dioxopyrazolidines.

3. It was shown that the alkylation of 4-monosubstituted derivatives of 1,2-diphenyl-3,5-dioxopyrazolidine with alkyl halides in the presence of 1% alcoholic potassium hydroxide solution gives the corresponding 4,4-disubstituted derivatives of 1,2-diphenyl-3,5-dioxopyrazolidine in 80-90% yields; the 4-methyl- and 4-ethyl-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidines were synthesized in this manner.

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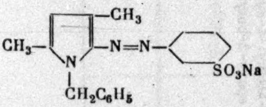
REACTION OF AMMONIA AND AMINES WITH OXIDES OF ACETYLENIC AND VINYLACETYLENIC SERIES

NEW METHOD FOR THE PREPARATION OF PYRROLE HOMOLOGS

F. Ia. Perveev and E. M. Kuznetsova

In a previous paper [1] we had shown that it is possible to go from α-amino alcohols of the acetylenic and vinylacetylenic series to the corresponding pyrrole derivatives. The objective in the present study was to determine the limits of application of this new method for the preparation of pyrroles as a function of the structural traits of the oxides and amines used. In addition, we attempted to find the conditions for the one-step synthesis of pyrroles by the reaction of ammonia and amines with oxides of the acetylenic and vinylacetylenic series.

As starting products we took the oxides listed in Table 1. To develop a one-step method for the preparation of pyrrole homologs directly from the corresponding oxides via their reaction with ammonia and amines we synthesized a number of previously known compounds (XI, XVI and XVIII) (Table 2). The properties of these substituted pyrroles and their derivatives (mercury complexes, phthalides) failed to differ from the literature data. Then, by reacting oxide (II) with methylamine, benzylamine, ethanolamine and aniline we obtained pyrroles (XII-XV). To prove the structure of the simplest of the synthesized compounds (XII) we subjected it to hydrolysis in alkaline medium in the presence of hydroxylamine hydrochloride [2]. The dioxime was isolated as a result of the hydrolysis. From N-benzyl-2,4-dimethylpyrrole (XIII) we obtained the azo dye (A). The reaction of methylamine with oxide (III) gave pyrrole (XVIII) in good yield. In order to obtain the α-phenyl-substituted pyrroles we studied the reaction of oxide (IV) with ethyl-, benzyl- and ethanolamines. The corresponding pyrroles (XIX-XXI) were isolated. A characteristic property of the α-phenylpyrroles is their poor reactivity with mercuric chloride. The initially formed white flocculent mercury derivative rapidly assumes various bright colors on standing in the air.



(A)

It seemed of interest to synthesize a pyrrole with a cyclohexene ring in the α-position, since such compounds are not described in the literature, and can hardly be obtained by any other method in one step. This synthesis was accomplished by reacting ethylamine with oxide (V). The isolated pyrrole is a quite unstable liquid that polymerizes easily and suffers much tarring even when distilled under a high vacuum, leading to a sharp reduction in the yield. We were unable to isolate the completely pure product in a yield exceeding 20-25%. The mercury derivative, the same as in the case of the α-phenyl-substituted pyrroles, is formed very slowly.

Of special interest is the synthesis of N-ethyl-4-methyl-2-vinylpyrrole (VI) and N-methyl-4-methyl-2-vinylpyrrole (VII), since a method for the preparation of such compounds has not existed up to now. An attempt to obtain vinylpyrroles by a one-step method proved unsuccessful, since the heating of oxide (I) with an excess of amine leads to closure of the pyrrole ring with the simultaneous addition of the amine to the double bond of the side chain.

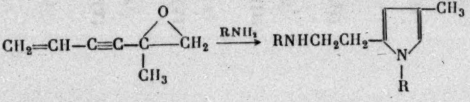


TABLE 1

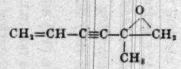
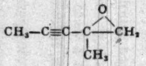
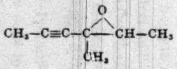
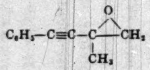
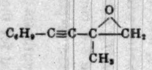
No.	Formula	Name	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D		Yield (in %)
						found	calc.	
(I)	 $CH_2{=}CH{-}C{\equiv}C{-}\underset{CH_3}{C}\overset{O}{\frown}CH_2$	2-Methyl-1,2-epoxy-5-hexen-3-yne	50—51° (15)	1.4739	0.9149	33.17	21.3	70
(II)	 $CH_3{-}C{\equiv}C{-}\underset{CH_3}{C}\overset{O}{\frown}CH_2$	2-Methyl-1,2-epoxy-3-pentyne	40—41 (22)	1.4461	0.9264	22.70	27.60	75
(III)	 $CH_3{-}C{\equiv}C{-}\underset{CH_3}{C}\overset{O}{\frown}CH{-}CH_3$	3-Methyl-2,3-epoxy-4-hexyne	43—44 (12)	1.4410	0.8856	32.84	32.56	75
(IV)	 $C_6H_5{-}C{\equiv}C{-}\underset{CH_3}{C}\overset{O}{\frown}CH_2$	2-Methyl-4-phenyl-1,2-epoxy-3-butyne	90—92 (2)	1.5552	1.0112	54.33	52.10	75
(V)	 $C_6H_9{-}C{\equiv}C{-}\underset{CH_3}{C}\overset{O}{\frown}CH_2$	2-Methyl-4-cyclohexenyl-1,2-epoxy-3-butyne	101—102 (2)	1.5274	0·9766	49.80	47.83	60

TABLE 2

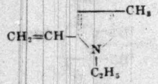
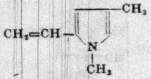
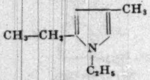
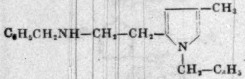
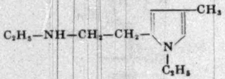
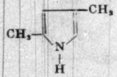
No.	Formula	Name	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D	
						found	calc.
(VI)		N-Ethyl-4-methyl-2-vinylpyrrole	35—36 (1)	1.5324	0.9170	44.20	45.60
(VII)		N-Methyl-4-methyl-2-vinylpyrrole	49 (1.5)	1.5380	0.9254	39.76	40.97
(VIII)		N-Ethyl-4-methyl-2-ethylpyrrole	43—45 (6)	1.4863	0.8852	44.56	44.46
(IX)		N-Benzyl-4-methyl-2-(β-benzylaminoethyl) pyrrole	135 (1.5)	1.5688	1.0154	96.38	98.36
(X)		N-Ethyl-4-methyl-2-(β-ethylaminoethyl) pyrrole	103—104 (0.5)	1.4950	0.9162	57.30	57.15
(XI)		2,4-Dimethylpyrrole	43 (2)	1.4950	0.9208	30.77	30.16

TABLE 2 (continued)

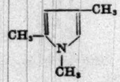
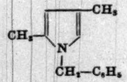
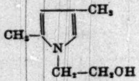
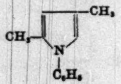
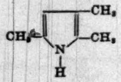
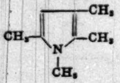
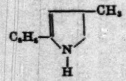
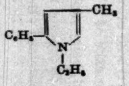
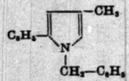
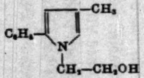
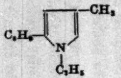
No.	Formula	Name	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D	
						found	calc.
(XII)		N-Methyl-2,4-dimethylpyrrole	39 (7)	1.4831	0.8914	35.33	34.94
(XIII)		N-Benzyl-2,4-dimethylpyrrole	142—145 (6)	1.5520	0.9985	59.43	59.52
(XIV)		N-Ethanol-2,4-dimethylpyrrole	83—85 (1)	1.5067	1.0116	41.59	41.02
(XV)		N-Phenyl-2,4-dimethylpyrrole	97—98 (0.5)	1.5800	1.0251	54.82	55.68
(XVI)		2,3,5-Trimethylpyrrole	45—46 (1.5)	1.4972	0.9300	34.22	34.32
(XVII)		N-Methyl-2,3,5-trimethylpyrrole	62—64 (5)	1.4899	0.9092	3990	3918

TABLE 2 (continued)

No.	Formula	Name	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D	
						found	calc.
(XVIII)		4-Methyl-2-phenylpyrrole	Crystals with m. p. 151-152°				
(XIX)		N-Ethyl-4-methyl-2-phenylpyrrole	90—91 (0.5)	1.5958	1.0249	59.44	61.46
(XX)		N-Benzyl-4-methyl-2-phenylpyrrole	151—153 (1)	1.6151	1.0732	77.19	79.52
(XXI)		N-Ethanol-4-methyl-2-phenylpyrrole	158—160 (1)	1.5913	1.0926	61.08	62.03
(XXII)		N-Ethyl-4-methyl-2-(α-cyclohexenyl)-pyrrole	102—105 (1)	1.5312	0.9621	60.37	60.89

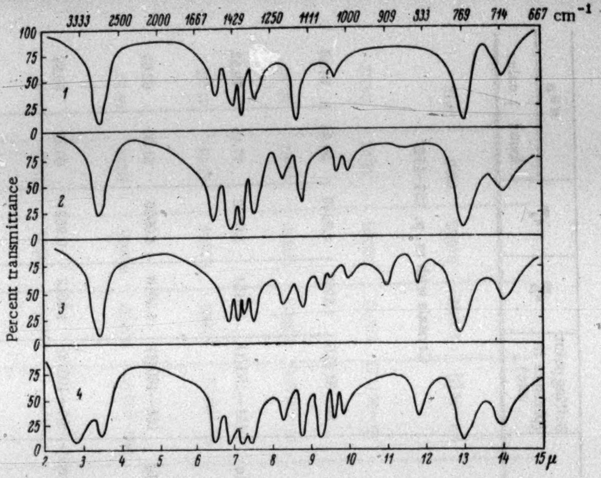
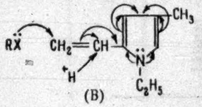


Fig. 1. Infrared absorption spectra. 1) 2,3,5-Trimethylpyrrole; 2) N-methyl-2,4-dimethylpyrrole; 3) N-ethyl-4-methyl-2-phenylpyrrole; 4) N-ethanol-2,4-dimethylpyrrole.

The reaction of ethylamine with 2-methyl-1,2-epoxy-5-hexen-3-yne gave N-ethyl-4-methyl-2-(β-ethylaminoethyl)-pyrrole (X). The order in which the ethylamine added to the side chain of the pyrrole was not shown conclusively. Nucleophilic substitution according to scheme (B) apparently occurs here.



(B)

After it was established that it is possible to add ethylamine to the side chain of vinylpyrroles it seemed obligatory to determine if it is possible to add amines with heavier radicals to the vinyl group. With this in mind we studied the reaction of oxide (I) with benzylamine. Here the reaction went with the formation of large amounts of tarry products and the yield of the pure pyrrole did not exceed 25%.

To obtain N-ethyl-4-methyl-2-vinylpyrrole (VI) and N-methyl-4-methyl-2-vinylpyrrole (VII) we used the amino alcohols 1-ethylamino-2-methyl-2-hydroxy-5-hexen-3-yne and 1-methylamino-2-methyl-2-hydroxy-5-hexen-3-yne, which were obtained by the reaction of oxide (I) with ethylamine and with methylamine in the cold. The indicated alcohols were heated in sealed tubes in the presence of a small amount of quinoline. After heating for 6 hrs the corresponding pyrroles (VI and VII) were isolated, being mobile light-yellow liquids with a characteristic pyrrole odor, insoluble in water and readible soluble in organic solvents, forming mercury derivatives, and giving a positive reaction with aqueous SeO_2 solution. The obtained vinyl-containing pyrroles polymerize on standing, and after several weeks are converted to a brittle glass.

To prove that a double bond is present in the side chain of N-ethyl-4-methyl-2-vinylpyrrole we subjected the compound to hydrogenation over Pt-catalyst. The amount of hydrogen absorbed corresponded to the amount theoretically required for the hydrogenation of one double bond. The product isolated from the hydrogenation was N-ethyl-4-methyl-2-ethylpyrrole (VIII), which gave characteristic pyrrole reactions with SeO_2 and mercuric chloride.

To prove the structure of pyrrole (VIII) we subjected it to hydrolysis in alkaline medium in the presence of hydroxylamine hydrochloride, and here the corresponding dioxime was isolated. The pyrroles synthesized by us are listed in Table 2. To prove the structure of the obtained compounds, besides chemical methods of study, we resorted to a study of the infrared absorption spectra of compounds (V-VII), (XII-XVII) and (XXIII). For this we used an IKS-11 infrared spectrometer with NaCl prism, operating in the 2-15 μ region.

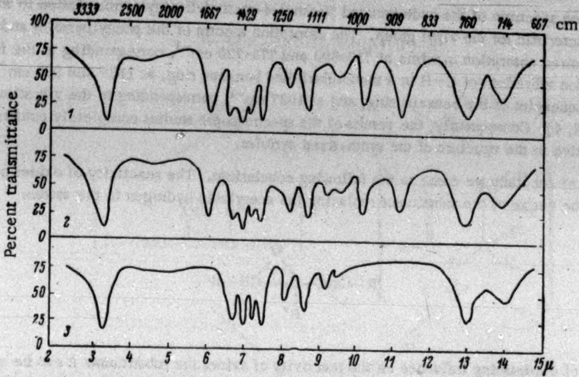


Fig. 2. Infrared absorption spectra. 1) N-Methyl-2-vinyl-4-methylpyrrole; 2) N-ethyl-2-vinyl-4-methylpyrrole; 3) N-ethyl-2-ethyl-4-methylpyrrole.

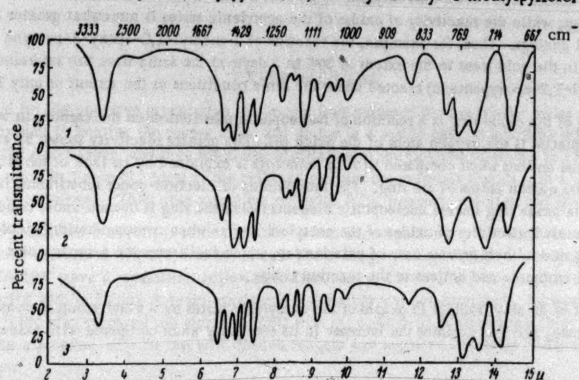


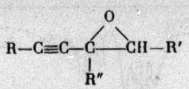
Fig. 3. Infrared absorption spectra. 1) N-Ethyl-4-methyl-2-phenylpyrrole; 2) N-benzyl-2,4-dimethylpyrrole; 3) N-benzyl-4-methyl-2-phenylpyrrole.

It was established that all of the investigated pyrroles are characterized by absorption maxima at 1530-1467, 1333 and 1144 cm^{-1}, corresponding to the vibration frequencies of the pyrrole ring; at 768 and 712 cm^{-1}, corresponding to the vibration frequencies of N–H and C–H in pyrrole; and at 2829 and 1492-1429 cm^{-1}, corresponding to the vibration frequencies of the CH_2 and CH_3 groups, which is in agreement with the literature data [3, 4]. In contrast to the alkyl-substituted pyrroles, the absorption spectrum of N-ethanol-2,4-dimethylpyrrole showed an absorption maximum at 3387 cm^{-1}, corresponding to the vibration frequency of the OH group. The absorption spectrum of N-ethyl-4-methyl-(α-cyclohexenyl) pyrrole showed an absorption band at 910 cm^{-1}, which apparently corresponds to the vibration frequency of C–C in the cyclohexane skeleton; the vibration frequency of the =CH bond in cyclohexene lies in the same region (Figs. 1-3).

In addition, the absorption spectra of the vinyl-substituted pyrroles showed absorption maxima at 1618 cm^{-1}, corresponding to the vibration frequency of the double bond in the side chain, and at 902-894 and 982 cm^{-1}, corresponding to the frequency of the nonplanar deformation vibration of the =C–H bond in the vinyl group.

The absorption spectrum of the hydrogenated N-ethyl-4-methyl-2-vinylpyrrole failed to show any absorption maxima characteristic for the vinyl group. The absorption spectra of the phenylpyrroles and N-benzyl-2,4-dimethylpyrrole showed absorption maxima at 710-690 and 770-730 cm^{-1}, corresponding to the frequencies of the nonpolar deformation vibrations of C—H in a monosubstituted benzene ring, at 1163 and 995 cm^{-1}, corresponding to the vibration frequencies of the benzene ring, and at 1037 cm^{-1}, corresponding to the vibration frequency of C—H in benzene [3, 4]. Consequently, the results of the spectroscopic studies completely confirm the chemical data obtained relative to the structure of the synthesized pyrroles.

On the basis of our study we came to the following conclusions. The reactivity of oxides of the acetylenic series depends on the nature of the substituent replacing the acetylenic hydrogen in the system



In the order of diminishing influence on the reactivity of oxides the substituents R can be arranged as follows: $CH_2{=}CH > C_6H_5 >$ alkyl > H.

From the literature it is known that ethylene oxide reacts with ammonia and amines much more rapidly than do its homologs, while the reactivity of oxides of the acetylenic series is somewhat greater than that of their saturated structural analogs. Thus, for example, the reaction of 2-methyl-1,2-epoxy-3-pentyne with 30% aqueous ammonia solution in the cold went to the extent of 30% in 3 days; at the same time the saturated oxide of similar structure (2-methyl-1,2-epoxypentane) reacted under the same conditions to the extent of only 10-12%.

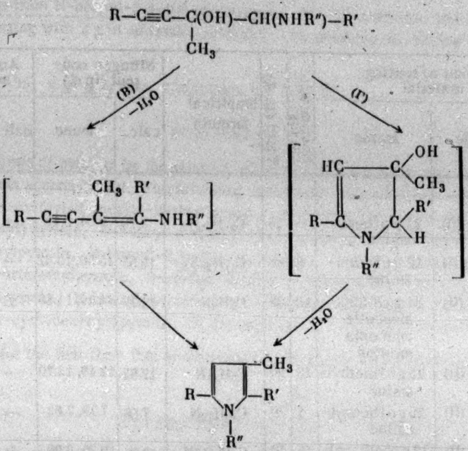
The opening of the oxide ring is a reaction of nucleophilic substitution on the carbon, in which connection the group being replaced is the oxygen atom of the oxide [5]. The greater reactivity shown by ethylene oxide toward ammonia and amines when compared with its homologs is explained by its lack of substituents, which donate electrons to the carbon atoms of the ring. The introduction of electron-donor substituents leads to decreasing the reactivity of the oxide ring toward nucleophilic reagents (when the ring is opened under conditions of alkaline catalysis). An increased reactivity of oxides of the acetylenic series when compared with homologs of ethylene oxide is apparently due to their greater ease of polarization, which facilitates the approach of a nucleophilic reagent of the type of ammonia and amines to the reaction center.

Replacement of an alkyl radical in oxides of the acetylenic series by a vinyl group increases the polarizability of the molecule, and this explains the increase in its reactivity when compared with oxides of the acetylenic series.

The same as in the case of unsymmetrical ethylene oxide homologs, the addition of ammonia, methyl-, ethyl- and benzylamines, ethanolamine and aniline to oxides of the acetylenic and vinylacetylenic series proceeds by the Krasuskii rule, i. e., the oxide ring is opened at the most highly hydrogenated carbon atom. Proof of this is the fact that the reaction of ammonia and amines with the indicated oxides leads to the formation of pyrroles, the synthesis of which can be depicted by either scheme (B) or (C) (see diagram on following page).

Such an order for the opening of an oxide ring is explained more by the electron structure of the molecule than by steric factors. It is known that the induction effect, spreading along a chain, gradually dies out. Consequently, it is natural for the carbon atom linked to a greater number of electron-donor groups to have a higher electron density than the adjacent carbon atom. From this it is clear that attack by a nucleophilic reagent will be directed first toward the carbon atom with the smaller electron density.

If a strong electron-acceptor substituent is present on a carbon atom of the oxide ring the order in which ammonia and amines add will be the reverse of the above, and depending on the strength of the substituent, either a mixture of isomers, as in the case of styrene oxide [6], or individual products of the reverse order of substitution, as in the case of glycidic acids [5], will be formed as the result of cleavage of the oxide ring.



EXPERIMENTAL

The method for the one-step preparation of pyrroles from oxides of the acetylenic series is an extremely simple one. It consists in heating the proper oxide and amine in a sealed tube on a boiling water bath, followed by separation of the water layer, and then fractional distillation of the isolated substance in vacuo (the experimental data are given in Table 3). Most of the obtained pyrroles are colorless liquids with a chloroform odor, turning yellow on storage. They give a positive test with SeO_2, mercuric chloride and Ehrlich reagent [7].

The mercury derivative of (XI) is white, and melts with decomposition at 135-137° (literature [8]: m. p. 136°). The mercury derivative of (XVI) had m. p. 109-110°. Long heating of (XI) with phthalic anhydride in acetic acid at 180-190° gave a crystalline yellow phthalide. M. p. 170-171° (literature [9]: m. p. 170°). The mixed melting point with authentic 2,4-dimethylpyrrole phthalide was not depressed. Substance (XI) gave a positive Ehrlich test. We also prepared the picrate of (XI) with m. p. 90.5-91.5° (literature [10]: 91-92°). Substance (XVI) did not form a picrate; also its test with Ehrlich reagent was negative. Pyrroles (XIII) and (XIV) show a slight fluorescence.

Hydrogenation of N-ethyl-4-methyl-2-vinylpyrrole. The hydrogenation was run over platinum catalyst in anhydrous alcohol solution. The amount of hydrogen consumed for 4 g of the compound was 760 ml (16.5°, 732.8 mm), or 684 ml of H_2 at 0° and 766 mm; the theoretical amount for the hydrogenation of one double bond is 664 ml of H_2. The hydrogenation product was dried over fused K_2CO_3, the alcohol distilled off, and the compound fractionally distilled in vacuo. We isolated 2.8 g of N-ethyl-4-methyl-2-ethylpyrrole, which gave characteristic pyrrole reactions with aqueous SeO_2 solution and with mercuric chloride.

Found %: N 10.15, 10.29. $C_9H_{15}N$. Calculated %: N 10.21.

Hydrolysis of N-ethyl-4-methyl-2-ethylpyrrole (VIII). A mixture of 2 g of (VIII), 2.55 g of $NH_2OH \cdot HCl$, 1.95 g of Na_2CO_3 and 20 g of 98% alcohol was heated for 10 hrs on the boiling water bath. The soda was filtered, and the alcohol was distilled off to a volume of 3 ml. The alcohol solution on cooling deposited a white crystalline precipitate of the dioxime, which was recrystallized from alcohol.

Found %: N 15.16, 15.10. $C_7H_{14}O_2N_2$. Calculated %: N 15.05.

Hydrolysis of N-methyl-2,4-dimethylpyrrole (XII). A mixture of 4 g of (XII), 5.1 g of $NH_2OH \cdot HCl$, 3.89 g of Na_2CO_3 and 40 g of 98% alcohol was heated for 11 hrs on the boiling water bath in a round-bottomed flask fitted with a reflux condenser. The soda was filtered, and then the alcohol was distilled off to a volume of 5 ml. The alcohol solution on cooling deposited a white crystalline precipitate of the dioxime, which after recrystallization from alcohol had m. p. 96-97°.

TABLE 3

No. of obtained pyrrole	Amount of starting material		Heating time (in hrs)	Yield (in %)	Empirical formula	Nitrogen content (in %)		Amount of active H	
	oxide	amine				calc.	found	calc.	found
(IX)	10 g(I)	23 g of benzylamine	18	25	$C_{21}H_{24}N_2$	9.19	9.04, 9.15	—	—
(X)	15 g (I)	16 g of ethylamine	6	68	$C_{11}H_{20}N_2$	15.55	15.50, 15.62	—	—
(XI)	10g (II)	25 g of 22% alcoholic ammonia solution	10	59	C_6H_9N	14.79	14.44, 14.65	1	0.98, 0.98
(XII)	10g (II)	15 g of methylamine	18	90	$C_7H_{11}N$	12.82	12.49, 12.70	—	—
(XIII)	10g (II)	15 g of benzylamine	1	70	$C_{13}H_{15}N$	7.56	7.78, 7.62	—	—
(XIV)	10 g (II)	10 g of ethanolamine	15	70	$C_8H_{13}ON$	10.06	10.25, 9.98	1	1.07, 1.01
(XV)	10 g (II)	20 g of aniline	17	63	$C_{12}H_{13}N$	8.18	8.30, 8.25	—	—
(VI)	14 g	1-ethylamino-2-methyl-2-hydroxy-5-hexen-3-yne and 1 g of quinoline	6	55	$C_9H_{13}N$	10.37	10.30, 10.40	—	—
(XVI)	10 g(III)	27 g of 22% alcoholic ammonia solution	9	64	$C_7H_{11}N$	12.83	12.64, 12.74	1	0.97, 1.06
(XVII)	10g (III)	5 g of methylamine	9	62	$C_8H_{13}N$	11.37	11.43, 11.13	—	—
(XVIII)	5 g (IV)	20 g of 20% alcoholic ammonia solution	10	50	$C_{11}H_{11}N$	8.90	8.73, 8.75	1	1.01, 1.01
(XIX)	5g (IV)	3 g of ethylamine	10	70	$C_{13}H_{15}N$	7.55	7.44, 7.61	—	—
(XX)	5g (IV)	7 g of benzylamine	10	75	$C_{18}H_{17}N$	5.66	6.78, 5.58	—	—
(XXI)	7g (IV)	5 g of ethanolamine	10	70	$C_{13}H_{15}ON$	6.95	7.10, 6.90	1	1.02, 1.01
(XXII)	10 g (V)	6 g of ethylamine	6	20	$C_{13}H_{19}N$	7.35	2.22, 7.29	—	—
(XXIII)	13 g	1-methylamino-2-methyl-2-hydroxy-5-hexen-3-yne and 0.5 ml of quinoline	6	75	$C_8H_{11}N$	11.55	11.32, 11.45	—	—

Note. For the structural formulas see Table 2.

Found %: N 19.61, 19.68. $C_6H_{12}O_2N_2$. Calculated %: N 19.44.

Preparation of azo dye from N-benzyl-2,4-dimethylpyrrole. The diazotization and azo-coupling were run in conventional manner (starting with 2 g of sulfanilic acid) [9]. The obtained red-yellow azo dye was recrystallized twice from water.

Found %: N 11.21, 10.85. $C_{19}H_{18}O_3N_3Na$. Calculated %: N 10.76.

SUMMARY

1. The one-step synthesis of pyrroles by the reaction of ammonia and amines with oxides of the acetylenic and vinylacetylenic series was accomplished. The following compounds were obtained with this method: N-ethyl-4-methyl-2-vinylpyrrole, N-methyl-4-methyl-2-vinylpyrrole, N-ethyl-4-methyl-2-ethylpyrrole, N-ethyl-4-methyl-2-(β-ethylaminoethyl) pyrrole, N-benzyl-4-methyl-2-(β-benzylaminoethyl) pyrrole, 2,4-dimethylpyrrole, N-methyl-2,4-dimethylpyrrole, N-benzyl-2,4-dimethylpyrrole, N-ethanol-2,4-dimethylpyrrole, N-phenyl-2,4-dimethylpyrrole, 2,3,5-trimethylpyrrole, N-methyl-2,3,5-trimethylpyrrole, 4-methyl-2-phenylpyrrole, N-ethyl-4-methyl-2-phenylpyrrole, N-benzyl-4-methyl-2-phenylpyrrole, N-ethanol-4-methyl-2-phenylpyrrole, and N-ethyl-4-methyl-2-(α-cyclohexenyl) pyrrole. Of the enumerated compounds 14 are new.

2. It was established for the first time that amines readily add to the double bond found in the side chains of a vinylpyrrole.

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TETRAACYLOXYSILANES IN ORGANIC SYNTHESIS

XVII. ACYLATION OF BENZENE WITH THE SILICOANHYDRIDES OF ACETIC, MONO-, DI- AND TRICHLOROACETIC AND β-BROMOPROPIONIC ACIDS

Iu. K. Iur'ev, Z. V. Beliakova, and V. P. Volkov

Two of us had described in previous papers the use of silicoanhydrides of monobasic and dibasic organic acids as convenient acylating agents in the Gustavson-Friedel-Crafts reaction for the respective preparation of ketones [1] and keto acids [2] of the benzene, thiophene and selenophene series. In connection with this it seemed of interest to determine the possibility of acylating the benzene and thiophene nuclei with the silicoanhydrides of ω-halo-substituted acids, and on the example of α- and β-halo acids to establish the relationship between the reaction course and the position and number of halogen atoms in the acid. With this in mind we reacted silicon tetrachloride in benzene medium with acetic, mono-, di- and trichloroacetic acids, and also with β-bromopropionic acid, and used the obtained silicoanhydrides to acylate benzene in the presence of anhydrous aluminum chloride.

The acylation of benzene with the acid chlorides of mono-, di- and trichloroacetic acids, and also of β-bromopropionic acid, is described in the literature. Thus, Rothstein and Saville [3] acylated benzene with chloroacetyl chloride and obtained chloroacetophenone in 87% yield; using dichloroacetyl chloride Gautier [4] obtained dichloroacetophenone; using trichloroacetyl chloride Biltz [5] obtained trichloroacetophenone (50%). According to Delacre [6], when the last reaction is run in excess benzene the product obtained is diphenylacetophenone – the alkylation product of two molecules of benzene with trichloroacetophenone.

Foreman and McElvain [7] obtained β-bromopropiophenone in 93% yield when they acylated benzene with β-bromopropionyl chloride in carbon disulfide medium.

In seeking the optimum conditions for the acylation of benzene with tetraacyloxysilanes we improved on the method for the acylation with silicoacetic anhydride and found that the yield of acetophenone could reach 80% if the mole ratio of aluminum chloride to acid, taken to obtain the silicoanhydride, was equal to 2 : 1, whereas with a 1.3 :1 ratio [8] the yield of acetophone is 47%.

In the present study we established that chloroacetic acid, reacting with silicon tetrachloride, forms silicochloroacetic anhydride, which when used to acylate benzene leads to the formation of chloroacetophenone in 45% yield when the $AlCl_3 : ClCH_2$ ratio = 2 : 1, and a 34% yield when the ratio = 1 : 1.

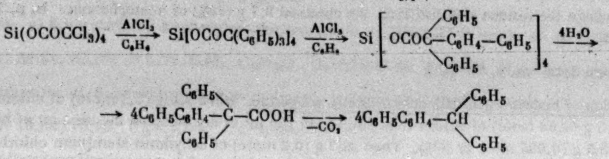
When benzene was acylated with silicodichloroacetic anhydride we obtained ω,ω-dichloroacetophenone in 25% yield.

$$4Cl_2CHCOOH + SiCl_4 \xrightarrow{C_6H_6} Si(OCOCHCl_2)_4 + 4HCl$$

$$4C_6H_6 + Si(OCOCHCl_2)_4 \xrightarrow{AlCl_3} 4C_6H_5COCHCl_2 + Si(OH)_4$$

When benzene was acylated with silicotrichloroacetic anhydride we obtained, instead of the expected trichloroacetophenone or diphenylacetophenone, a small amount of p-benzhydryldiphenyl. It is possible to explain the formation of the latter by the alkylation of benzene with silicotrichloroacetic anhydride, which led to the formation of the silicoanhydride of triphenylacetic acid. One of the benzene rings of the triphenylacetic silicoanhydride formed in this manner then condenses (under the influence of aluminum chloride) with benzene, giving the silicoanhydride of biphenyldiphenylacetic acid, which on hydrolysis gives the acid itself. The biphenyldiphenylacetic acid suffers decarboxylation when distilled, and this yields p-benzhydryldiphenyl.

$$4CCl_3COOH + SiCl_4 \longrightarrow Si(OCOCCl_3)_4 + 4HCl$$



$$Si(OCOCCl_3)_4 \xrightarrow[C_6H_6]{AlCl_3} Si[OCOC(C_6H_5)_3]_4 \xrightarrow[C_6H_6]{AlCl_3} Si\left[OCOC(C_6H_5)_2{-}C_6H_4{-}C_6H_5\right]_4 \xrightarrow{4H_2O}$$

$$\longrightarrow 4C_6H_5C_6H_4{-}C(C_6H_5)_2{-}COOH \xrightarrow[-CO_2]{} 4C_6H_5C_6H_4{-}CH(C_6H_5)_2$$

We determined the extent to which the silicoanhydrides of the chloroacetic acids were formed by the amount of hydrogen chloride evolved, and found that in benzene medium they are formed in nearly quantitative yield.

Consequently, the results obtained in the acylation of benzene with the silicoanhydrides of acetic, mono-, di- and trichloroacetic acids permit stating the following rule as regards their behavior in the Gustavson-Friedel-Crafts reaction: the stronger the acid contained in the silicoanhydride, the greater is the stability of the latter and the weaker is its acylating capacity.

This rule is also supported by the fact that the acylation of thiophene with silicochloroacetic anhydride, which we attempted to run in the presence of anhydrous stannic chloride, did not go at all, whereas when the acylation was run with silicoacetic anhydride under the same conditions we obtained acetothienone in 94% yield [1].

The acylation of benzene with the silicoanhydride of β-bromopropionic acid, using a molar ratio of $AlCl_3 : BrCH_2CH_2COOH = 2:1$, gave higher yields of the reaction products, reaching 90%. However, even when the reaction mass was decomposed with a mixture of ice and concentrated hydrochloric acid we obtained only β-hydroxypropiophenone (57%), being the hydrolysis product of the β-bromopropiophenone formed in the reaction, and β-phenylpropiophenone (33%), the latter being the product of the alkylation of benzene with the β-bromopropiophenone formed during the reaction

$$4C_6H_6 + Si(OCOCH_2CH_2Br)_4 \xrightarrow[C_6H_6]{AlCl_3} 4C_6H_5COCH_2CH_2Br + Si(OH)_4$$

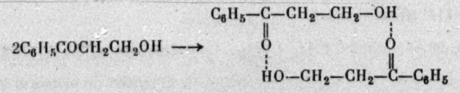
$$C_6H_5COCH_2CH_2Br \xrightarrow[-HBr]{H_2O} C_6H_5COCH_2CH_2OH$$

$$C_6H_5COCH_2CH_2Br + C_6H_6 \xrightarrow{AlCl_3} C_6H_5COCH_2CH_2C_6H_5 + HBr$$

When the above reaction was run under the same conditions, but with the $AlCl_3 : BrCH_2CH_2COOH$ ratio = 1 : 1, we obtained β-bromopropiophenone in 70% yield.

When the acylation was run in nitrobenzene medium we obtained only β-hydroxypropiophenone (34%).

In the distillation of β-hydroxypropiophenone there occurred not only cleavage of water with the formation of vinyl phenyl ketone [9], but also polymerization with the formation of a crystalline substance, which proved to be a dimer in which two molecules of β-hydroxypropiophenone are apparently connected to each other through two hydrogen bonds.



$$2C_6H_5COCH_2CH_2OH \longrightarrow \begin{array}{c} C_6H_5{-}C({=}O){-}CH_2{-}CH_2{-}OH \\ \vdots \qquad\qquad \vdots \\ HO{-}CH_2{-}CH_2{-}C({=}O){-}C_6H_5 \end{array}$$

EXPERIMENTAL

Acylation of benzene with silicoacetic anhydride. Silicoacetic anhydride was obtained by the general method, described earlier [1], from 6 g (0.1 mole) of acetic acid and 5 g (0.03 mole) of silicon tetrachloride in 150 ml of dry benzene. Then 26.7 g (0.2 mole) of anhydrous aluminum chloride was added in 20 min at 20° and the mixture heated for 5 hrs on the water bath, with gradual elevation of the temperature (the last 30 min on a boiling water bath). The mixture was cooled and poured with stirring over 250 g of ice. The benzene was steam-distilled, while the acetophenone was distilled with superheated steam. After separating the benzene layer the water layer was extracted with ether. The extracts were combined and dried over calcium chloride. After distilling off the ether and benzene the residue was distilled. We obtained 9.7 g (80%) of acetophenone: b. p. 71-72° (7 mm); m. p. 19.5-20°.

Literature data: m. p. 20° [10].

Acylation of benzene with silicochloroacetic anhydride. When 9.5 g (0.1 mole) of chloroacetic acid was reacted with 5 g (0.03 mole) of silicon tetrachloride in 150 ml of dry benzene the amount of hydrogen chloride evolved was 3.5 g (0.095 mole or 95%). Then 26.7 g (0.2 mole) of anhydrous aluminum chloride was added in small portions over a period of 3 hrs at 20°, and the mixture heated as indicated above. The chloroacetophenone after distillation with superheated steam was extracted with benzene and dried over calcium chloride. After distilling off the benzene the residue was distilled. We obtained 7 g (45%) of chloroacetophenone with b. p. 101.5-102.5° (5 mm) and m. p. 57-57.5° (from alcohol). Semicarbazone: m. p. 155-156° (from alcohol).

With a mole ratio of $AlCl_3 : ClCH_2COOH = 1:1$, the reaction of 19 g of chloroacetic acid and 10 g of silicon tetrachloride in 250 ml of dry benzene with 29.5 g of aluminum chloride gave 10.5 g (34%) of chloroacetophenone with m. p. 57-57.5° (from alcohol).

Both of the above preparations when mixed with authentic chloroacetophenone failed to depress the melting point.

Literature data: m. p. 57-58° [11]; m. p. 56° [12]. Semicarbazone: m. p. 156° [13].

Acylation of benzene with silicodichloroacetic anhydride. This acylation was run in the same manner as the acylation with silicoacetic anhydride. The reaction of 12. 9 g (0.1 mole) of dichloroacetic acid with 5 g (0.03 mole) of silicon tetrachloride in 150 ml of dry benzene resulted in the evolution of 3.62 g (99%) of hydrogen chloride. Then 26.7 g (0.2 mole) of anhydrous aluminum chloride was added, the mixture heated as already described, the reaction mass decomposed with ice and concentrated hydrochloric acid, then filtered (suction-filtration through cotton cloth), and the reaction products isolated (by distillation) from the benzene solution and the ether extract of the precipitate. We obtained: a) 5.9 g (46%) of dichloroacetic acid, and b) 4.75 g (25%) of ω,ω-dichloroacetophenone.

B. p. 80-82° (2 mm), $n^{20}D$ 1.5618, d_4^{20} 1.3392, MR_D 45.78. $C_8H_6OCl_2F_3$. Calculated 45.29. Found %: Cl 37.55, 37.29. $C_8H_6OCl_2$. Calculated %: Cl 37.50. Literature data [4]: b. p. 143° (25 mm), d^{16} 1.340.

With a mole ratio of $AlCl_3 : Cl_2CHCOOH = 1:1$, the reaction of 12.9 g of dichloroacetic acid and 5 g of silicon tetrachloride in 150 ml of dry benzene with 15 g (0.11 mole) of aluminum chloride gave: a) 6.5 g (50%) of dichloroacetic acid, and b) 4.6 g (24.0%) of ω,ω-dichloroacetophenone with b. p. 80-82° (2 mm), and $n^{20}D$ 1.5618.

The acylation of benzene with silicotrichloroacetic anhydride was run in the same manner as already described for acylation with silicoacetic anhydride. The reaction of 16.4 g (0.1 mole) of trichloroacetic acid with 5 g (0.03 mole) of silicon tetrachloride in 150 ml of dry benzene resulted in the evolution of 3.3 g (90%) of hydrogen chloride. Then 15 g (0.11 mole) of anhydrous aluminum chloride was added, the mixture heated as usual, the reaction mass decomposed with ice and concentrated hydrochloric acid, then filtered (suction-filtration through cotton cloth), and the reaction products isolated (by distillation) from the benzene solution and the ether extract of the precipitate. We obtained: a) 7.36 g (45.0%) of trichloroacetic acid, and b) 1.6 g (5%) of p-benzylhydryl-diphenyl with m. p. 113-114° (from alcohol).

Found %: C 93.67, 93.58; H 6.39, 6.44. $C_{25}H_{20}$. Calculated %: C 93.71; H 6.29. Literature data [14]: m. p. 112-113°.

The residue in the distillation flask was treated with caustic solution, filtered, and the filtrate extracted with ether. The alkaline solution was acidified, and the obtained precipitate, being biphenyldiphenylacetic acid (0.1 g), was filtered. The compound had m. p. 218-220°. Literature data [15]: m. p. 220-222°.

Acylation of benzene with the silicoanhydride of β-bromopropionic acid. 1) The synthesis was run in the same manner as in the acylation with silicoacetic anhydride. For reaction we took 150 ml of dry benzene, 15.3 g (0.1 mole) of β-bromopropionic acid, 5 g (0.03 mole) of silicon tetrachloride and 26.7 g (0.2 mole) of anhydrous aluminum chloride. The reaction mass after decomposition with ice and concentrated hydrochloric acid was filtered (suction-filtration through cotton cloth), and the reaction products were isolated (by distillation) from the benzene solution and the ether extract of the precipitate.

We obtained: a) 6.9 g (33%) of β-phenylpropiophenone: b. p. 154-156° (4 mm); m. p. 71.5-72°.

Found %: C 85.84, 86.07; H 6.77, 6.86. $C_{15}H_{14}O$. Calculated %: C 85.71; H 6.67.

The semicarbazone of β-phenylpropiophenone had m. p. 143-143.5° (from alcohol).

Found %: N 16.00, 16.03. $C_{16}H_{17}ON_3$. Calculated %: N 15.72.

The 2,4-dinitrophenylhydrazone of β-phenylpropiophenone had m. p. 182-183° (from ethyl acetate).

Found %: N 14.28, 14.33. $C_{21}H_{18}O_4N_4$. Calculated %: N 14.35. Literature data: m. p. 72-73° [16]; semicarbazone: m. p. 143° [17]; 2,4-dinitrophenylhydrazone: m. p. 166° [18].

b) We also obtained 8.55 g (57%) of β-hydroxypropiophenone.

B. p. 120-124° (4 mm), $n^{20}D$ 1.5365, d_4^{20} 1.1078, MR_D 42.31. $C_9H_{10}O_2F_3$. Calculated: 41.69. Literature data: b. p. 143-144° (20 mm) [9], $n^{20}D$ 1.5332, d_4^{20} 1.0983, MR_D 42.43 [19].

Water was cleaved when β-hydroxypropiophenone was reacted with semicarbazide [9] and vinyl phenyl ketone was formed, as a result of which the corresponding semicarbazone was obtained with m. p. 227-227.5° (with decomp.) (from butyl alcohol).

Found %: C 63.16, 63.01; H 5.82, 5.77; N 21.74, 21.89. $C_{10}H_{11}ON_3$. Calculated %: C 63.46; H 5.86; N 22.20.

Redistillation of the β-hydroxypropiophenone also resulted in the cleavage of water and the resulting substance (b. p. 88-89° at 9 mm) when reacted with bromine in carbon disulfide gave a dibromide with m. p. 57-57.5° (from petroleum ether), being α,β-dibromoethyl phenyl ketone.

Found %: Cr 54.69, 54.59. $C_9H_8OBr_2$. Calculated %: Br 54.74. Literature data: vinyl phenyl ketone, b. p. 111-112° [9]; dibromide, m. p. 53.5-54° [20]; m. p. 58° [21].

The major portion of the β-hydroxypropiophenone formed a dimer, which was obtained as white crystals with m. p. 48.5-49° (from petroleum ether).

Found %: C 71.62, 71.63; H 6.88, 6.97. M 297, 308 (cryoscopically in benzene). $C_{18}H_{20}O_4$. Calculated %: C 71.96; H 6.71. M 300.

2) For reaction we took 150 ml of dry benzene, 20 g (0.13 mole) of β-bromopropionic acid, 7.5 g (0.04 mole) of silicon tetrachloride and 20 g (0.15 mole) of anhydrous aluminum chloride. We obtained 19.5 g (70%) of β-bromopropiophenone with m. p. 59-60° (from petroleum ether).

Found %: Br 37.43. C_9H_9OBr. Calculated %: Br 37.55. Literature data: m. p. 59-60° [22]; m. p. 58-59° [7].

3) From 15.3 g of β-bromopropionic acid, 5 g of silicon tetrachloride and 7.8 g of dry benzene in 150 ml of dry nitrobenzene, in the presence of 26.7 g of aluminum chloride, we obtained 5 g (34%) of β-hydroxypropiophenone: b. p. 128-133° (12 mm), $n^{20}D$ 1.5359.

SUMMARY

1. Based on the acylation of benzene with the silicoanhydrides of acetic, chloroacetic, dichloroacetic and trichloroacetic acids in the presence of anhydrous aluminum chloride it was established that the stronger the acid forming the silicoanhydride, the greater the stability of the latter and the weaker its acylating capacity.

2. The acylation of benzene with silico-β-bromopropionic anhydride gave β-bromopropiophenone in good yield.

3. When the acylation of benzene with silico-β-bromopropionic anhydride is run under certain conditions the mobility of the halogen atom in the formed β-bromopropiophenone leads, on the one hand, to alkylation of the benzene ring by the β-bromopropiophenone, and on the other hand, to easy hydrolysis during decomposition of the complex, as a result of which the reaction products prove to be β-phenylpropiophenone and β-hydroxypropiophenone.

4. β-Hydroxypropiophenone when distilled forms a dimer with the composition $C_{18}H_{20}O_4$.

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ETHYLENE SULFIDE IN THE SYNTHESIS OF HETEROCYCLIC COMPOUNDS WITH TWO HETERO ATOMS

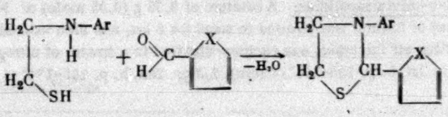
VIII. SYNTHESIS OF 2-(2-FURYL)-, 2-(2-THIENYL)-, AND 2-(2-SELENIENYL)-3-ARYLTHIAZOLIDINES

Iu. K. Iur'ev and S. V. Diatlovitskaia

In previous papers [1-3] we have shown that the condensation of N-(β-mercaptoethyl)-arylamines with aldehydes leads to the formation of 2-alkyl- (or aryl)-3-arylthiazolidines. Since the reaction with benzaldehyde goes easily, then it could be expected that other aldehydes of an aromatic character, as for example, furfural, 2-thiophenecarboxaldehyde and 2-selenophenecarboxaldehyde, would condense with N-(β-mercaptoethyl)-arylamines to form the corresponding thiazolidines.

From the literature it is known that S. V. Tsukerman [4] attempted to condense cysteine hydrochloride with furfural. However, the formation of 2-(2-furyl)-thiazolidine failed to occur here: only the furfural mercaptal was obtained when the reaction was run in alcohol medium, while in aqueous medium the substance obtained was free of sulfur.

In the present paper we condensed furfural, 2-thiophenecarboxaldehyde and 2-selenophenecarboxaldehyde with N-(β-mercaptoethyl)-arylamines and obtained the corresponding series of thiazolidines: 2-(2-furyl)-2-arylthiazolidines, 2-(2-thienyl)-3-arylthiazolidines and 2-(2-selenienyl)-3-arylthiazolidines.



$Ar = C_6H_5$; p- & o-$CH_3C_6H_4$; p- & o-$CH_3OC_6H_4$.
X = O, S, Se.

It should be mentioned that the 2-(2-furyl)-3-arylthiazolidines are quite unstable compounds: they are easily decomposed when vacuum-distilled, and also when treated with concentrated hydrochloric acid or hydrogen chloride, which makes it impossible to obtain their hydrochlorides. 2-(2-Furyl)-3-o-anisylthiazolidine proved to be so unstable that we were unable to obtain it in the pure state or to characterize it. It is probable that the instability of this type of compound was the reason for the failure of the above described attempts to synthesize 2-(2-furyl)-thiazolidine [4].

The 2-(2-thienyl)- and 2-(2-selenienyl)-3-arylthiazolidines proved to be more stable compounds: they are decomposed only when boiled with concentrated hydrochloric acid for 10-15 min.

The reactivity of the ortho-benzene-substituted isomers of the N-(β-mercaptoethyl)-arylamines in the above-described reactions was poorer than that of the corresponding para-isomers, which is in agreement with earlier made observations [2, 5, 6]. Thus, when N-(β-mercaptoethyl)-o-toluidine and N-(β-mercaptoethyl)-o-anisidine were condensed with furfural, 2-thiophenecarboxaldehyde and 2-selenophenecarboxaldehyde the yields of the thiazolidines were lower than the yields of the corresponding thiazolidines, obtained using N-(β-mercaptoethyl)-p-toluidine and N-(β-mercaptoethyl)-p-anisidine in the condensation.

EXPERIMENTAL*

Reaction of N-(β-Mercaptoethyl)-arylamines with Furfural

2-(2-Furyl)-3-phenylthiazolidine. A mixture of 7.65 g (0.05 mole) of N-(β-mercaptoethyl)-aniline and 4.8 g (0.05 mole) of furfural was boiled in 30 ml of dry benzene in a Dean-Stark apparatus until water ceased to come over in the distillate. The amount of water collected was 0.85 ml. After distilling off the benzene the oily residue was shaken with 5 ml of alcohol and 25 ml of saturated sodium bisulfite solution. The precipitate of bisulfite derivative was filtered and washed with ether. The filtrate was extracted 3 times with ether, and the combined ether extracts were dried over anhydrous magnesium sulfate.

After removal of the ether by distillation the oily residue was vacuum-distilled in a stream of nitrogen (slight decomposition). After distilling off several drops of a crimson-colored liquid the fraction with b. p. 175-180° (3 mm) was collected. This fraction, weighing 8 g (69%), was 2-(2-furyl)-3-phenylthiazolidine, and after redistillation had the following constants.

B. p. 175-176° (3 mm), $n^{20}D$ 1.6280, d_4^{20} 1.2167, MR_D 67.47. $C_{13}H_{13}ONS$ F_5. Calculated 66.85. Found %: C 66.90, 66.88; H 5.80, 5.68; N 6.03, 6.04. $C_{13}H_{13}ONS$. Calculated %: C 67.50; H 5.67; N 6.06.

2-(2-Furyl)-3-p-tolylthiazolidine. A mixture of 8.35 g (0.05 mole) of N-(β-mercaptoethyl)-p-toluidine and 4.8 g (0.05 mole) of furfural was allowed to stand at room temperature for 4 hrs, and then worked up in the same manner as described above. After distilling off the ether from the ether extract of the reaction product the residue crystallized and was 2-(2-furyl)-3-p-tolylthiazolidine: m. p. 56.5-57.5° (from alcohol). Yield 9.4 g (76.5%).

Found %: C 68.68, 68.50; H 6.12, 6.30; N 5.66, 5.76. $C_{14}H_{15}ONS$. Calculated %: C 68.54; H 6.16; N 5.71.

2-(2-Furyl)-3-p-anisylthiazolidine. From 9.15 g (0.05 mole) of N-(β-mercaptoethyl)-p-anisidine and 4.8 g (0.05 mole) of furfural, using the procedure of the preceding experiment, we obtained 11.7 g (86.5%) of 2-(2-furyl)-3-p-anisylthiazolidine: m. p. 75.5-76° (from alcohol).

Found %: C 64.52, 64.39; H 5.89, 5.87; N 5.38, 5.43. $C_{14}H_{15}O_2NS$. Calculated %: C 64.34; H 5.79; N 5.36.

2-(2-Furyl)-3-o-tolylthiazolidine. A mixture of 8.35 g (0.05 mole) of N-(β-mercaptoethyl)-o-toluidine and 4.8 g (0.05 mole) of furfural was allowed to stand for 6 hrs, and then worked up as described above. The oil, obtained after distilling off the ether, was vacuum-distilled in a stream of nitrogen, and here the following fractions were collected: 1st, b. p. 135-145° (4 mm), 1.3 g; 2nd, b. p. 145-174° (4 mm), 2.42 g; 3rd, b. p. 174-180° (4 mm), 3.8 g.

The 1st fraction was unreacted N-(β-mercaptoethyl)-o-toluidine; the 2nd fraction was a mixture of the unreacted amine and 2-(2-furyl)-3-o-tolylthiazolidine; the 3rd fraction was 2-(2-furyl)-3-o-tolylthiazolidine.

Redistillation of the 2nd and 3rd fractions gave 5.1 g (41%) of 2-(2-furyl)-3-o-tolylthiazolidine.

B. p. 180-182° (4 mm), $n^{20}D$ 1.6032, d_4^{20} 1.1800, MR_D 71.43. $C_{14}H_{15}ONS$ F_5. Calculated 71.47. Found %: C 68.61, 68.74; H 6.24, 6.26; N 6.07. $C_{14}H_{15}ONS$. Calculated %: C 68.54; H 6.16; N 5.71.

Reaction of N-(β-Mercaptoethyl)-arylamines with 2-Thiophenecarboxaldehyde

A mixture of 0.01 g mole of N-(β-mercaptoethyl)-arylamine and 0.01 g mole of 2-thiophenecarboxaldehyde was allowed to stand at room temperature for 20 hrs. [In the case of N-(β-mercaptoethyl)-o-toluidine and N-(β-mercaptoethyl)-p-carbethoxyaniline the mixtures were allowed to stand for 40 hrs.]

The crystals of 2-(2-thienyl)-3-arylthiazolidine were filtered and recrystallized from 80% alcohol.

The constants of the 2-(2-thienyl)-3-arylthiazolidines obtained in the indicated manner are listed in Table 1.

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* Student G. P. Aleksandrova assisted in the experimental portion of this study.

TABLE 1

2-(2-Thienyl)-3-arylthiazolidines

Name of obtained compounds	Melting point	Yield		Analysis data					
				C		H		N	
		in g	in %	found	calc.	found	calc.	found	calc.
2-(2-Thienyl)-3-phenylthiazolidine	70.5—71°	2.0	80	63.42, 63.34	63.11	5.45, 5.41	5.30	5.78, 5.89	5.66
2-(2-Thienyl)-3-o-tolylthiazolidine	34.5—35	0.53	20	64.34, 64.29	64.32	5.96, 5.91	5.78	5.31, 5.39	5.36
2-(2-Thienyl)-3-p-tolylthiazolidine	72.5—73	2.6	100	64.17, 64.14	64.32	5.81, 5.91	5.78	5.51, 5.67	5.36
2-(2-Thienyl)-3-o-anisylthiazolidine	74.5—75	1.7	61.5	61.04, 60.87	60.61	5.69, 5.69	5.45	5.28, 5.05	5.05
2-(2-Thienyl)-3-p-anisylthiazolidine	77—77.5	2.75	100	60.67, 60.51	60.61	5.56, 5.61	5.45	5.30, 5.15	5.05
2-(2-Thienyl)-3-p-carbethoxyphenylthiazolidine	105.5—106	1.53	48	59.94, 60.04	60.15	5.23, 5.34	5.36	4.50, 4.48	4.39

Reaction of N-(β-Mercaptoethyl)-arylamines with 2-Selenophenecarboxaldehyde

Mixtures of 0.01 mole of N-(β-mercaptoethyl)-arylamine and 0.01 mole of 2-selenophenecarboxaldehyde were allowed to stand for 20 hrs.

In the case of N-(β-mercaptoethyl)-p-toluidine and N-(β-mercaptoethyl)-o-anisidine the mixtures were allowed to stand for 48 hrs, after which the reaction products were dissolved in ether, and the solutions dried over anhydrous magnesium sulfate; after distilling off the ether the residues crystallized.

The crystals of 2-(2-selenienyl)-3-arylthiazolidine were filtered and recrystallized from 80% alcohol.

The constants of the 2-(2-selenienyl)-3-arylthiazolidines obtained in the indicated manner are listed in Table 2.

TABLE 2

2-(2-Selenienyl)-3-arylthiazolidines

Name of obtained compounds	Melting point	Yield		Analysis data					
				C		H		N	
		in g	in %	found	calc.	found	calc.	found	calc.
2-(2-Selenienyl)-3-phenylthiazolidine	65.5—66°	1.54	52.5	53.33, 53.37	53.06	4.68, 4.59	4.45	4.98, 4.92	4.75
2-(2-Selenienyl)-3-o-tolylthiazolidine	56—56.5	1.67	54	54.68, 54.58	54.54	5.13, 5.15	4.91	4.80, 4.63	4.54
2-(2-Selenienyl)-3-p-tolylthiazolidine	81.5—82	1.9	61	54.24, 54.43	54.54	5.07, 5.09	4.91	4.85, 4.64	4.54
2-(2-Selenienyl)-3-o-anisylthiazolidine	96.5—97	1.73	52.5	51.70, 51.91	51.85	4.77, 4.69	4.66	4.55, 4.49	4.32
2-(2-Selenienyl)-3-p-anisylthiazolidine	81—81.5	2.95	91	51.68, 51.71	51.85	4.85, 4.93	4.66	4.45, 4.39	4.32

SUMMARY

1. The condensation of N-(β-mercaptoethyl)-arylamines with furfural gave the previously unknown 2-(2-furyl)-3-phenyl-, 2-(2-furyl)-3-o-tolyl-, 2-(2-furyl)-3-p-tolyl- and 2-(2-furyl)-3-p-anisylthiazolidines.

2. The condensation of N-(β-mercaptoethyl)-arylamines with 2-thiophenecarboxaldehyde gave the previously unknown 2-(2-thienyl)-3-phenyl-, 2-(2-thienyl)-3-o-tolyl-, 2-(2-thienyl)-3-p-tolyl-, 2-(thienyl)-3-o-anisyl-, 2-(2-thienyl)-3-p-anisyl- and 2-(2-thienyl)-3-p-carbethoxyphenylthiazolidines.

3. The condensation of N-(β-mercaptoethyl)-arylamines with 2-selenophenecarboxaldehyde gave the previously unknown 2-(2-selenienyl)-3-phenyl-, 2-(2-selenienyl)-3-o-tolyl-, 2-(2-selenienyl)-3-p-tolyl-, 2-(2-selenienyl)-3-o-anisyl- and 2-(2-selenienyl)-3-p-anisylthiazolidines.

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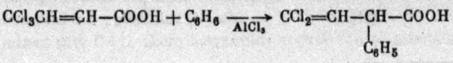
CONDENSATION OF γ,γ,γ-TRICHLOROCROTONONITRILE WITH BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE

A. D. Grebeniuk and I. P. Tsukervanik

In studying the influence exerted by the stability of the intermediate complex with aluminum chloride on the reactivity of α,β-unsaturated nitriles it was shown by us [1] that γ,γ,γ-trichlorocrotononitrile reacts readily with benzene in the presence of 1.2 g-moles of $AlCl_3$. The high reactivity of this nitrile when compared with that of acrylonitrile was explained by us as being due to the influence exerted by the trichloromethyl group, which reduces the stability of the intermediate complex. As a result of reaction we obtained a 63% yield of phenyldichlorovinylacetonitrile, proved by saponification to phenylsuccinic acid. The position of the phenyl group was not determined, since on the basis of some literature data [2, 3] we assumed that the manner in which benzene adds to the double bond will be determined by the conjugation effect of the double bond with the nitrile group. Proceeding from these considerations, the reaction product was assigned the structure of β-phenyldichlorovinylacetonitrile (I).

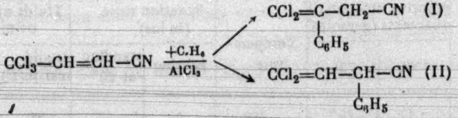
Recently A. N. Nesmeianov, L. I. Zakharkin and R. Kh. Friedlina [4], studying the effect of σ,π-conjugation in unsaturated compounds containing a trichloromethyl group, showed that the condensation of γ,γ,γ-trichlorocrotonic acid with benzene in the presence of aluminum chloride leads to the formation of α-phenyldichlorovinylacetic acid.



$$CCl_3CH{=}CH{-}COOH + C_6H_6 \xrightarrow[AlCl_3]{} CCl_2{=}CH{-}\underset{\displaystyle C_6H_5}{\underset{|}{CH}}{-}COOH$$

This new information, testifying to the great power exerted by the conjugation of a CCl_3 group with a double bond, made it necessary to determine the position of the phenyl group in the product obtained by us when γ,γ,γ-trichlorocrotononitrile was condensed with benzene.

Depending on whether the trichloromethyl or the phenyl group exerts predominant influence on the double bond it is possible to obtain either α-phenyldichlorovinylacetonitrile (II) or β-phenyldichlorovinylacetonitrile (I), according to the scheme

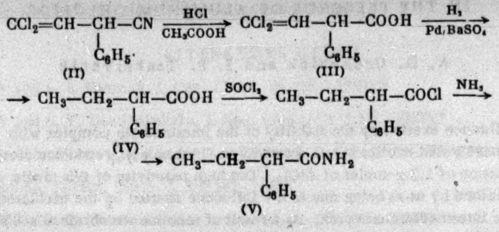


$$CCl_3{-}CH{=}CH{-}CN \xrightarrow[AlCl_3]{+C_6H_6} \begin{cases} CCl_2{=}\underset{\displaystyle C_6H_5}{\underset{|}{C}}{-}CH_2{-}CN & (I) \\ CCl_2{=}CH{-}\underset{\displaystyle C_6H_5}{\underset{|}{CH}}{-}CN & (II) \end{cases}$$

Together with a study of the condensation product, we made a more detailed study of the influence of reaction conditions on the condensation course. We were able to show that the reaction also goes in the absence of excess catalyst, using only 0.8-0.9 g-mole of $AlCl_3$. This again testifies to the high reactivity shown by γ,γ,γ-trichlorocrotononitrile. However, reducing the amount of catalyst leads to a sharp reduction in the reaction rate: if at 60-70° and a reaction time of 2-4 hrs the yield of phenyldichlorovinylacetonitrile using 1.2 g-moles of $AlCl_3$ is 62-63%, then with 0.8 g-mole of catalyst the yield of product drops to 23%, despite the fact that the reaction time is increased to 16 hrs.

Further it was established that the main reaction product, boiling in the range 130-132° at 6 mm, and 140-145° at 8 mm, is not homogeneous. Instead it consists of a mixture of two nitriles – one a liquid and the other being crystalline with m. p. 92-92.5°. The amount of either nitrile in the mixture depends on the reaction conditions. The relative amount of the crystalline nitrile increases with decrease in the amount of $AlCl_3$.

The liquid nitrile is α-phenyldichlorovinylacetonitrile (II). Its structure was proved in the following manner: the nitrile was saponified with a mixture of hydrochloric and acetic acids to α-phenyldichlorovinylacetic acid (III), which by hydrogenation over palladium was converted to α-phenylbutyric acid (IV), identified by the mixed melting point of its amide with the amide of α-phenylbutyric acid, obtained by a counter synthesis.

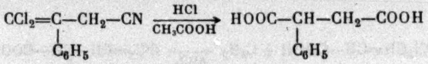


$$\underset{(II)}{CCl_2{=}CH-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CN} \xrightarrow[CH_3COOH]{HCl} \underset{(III)}{CCl_2{=}CH-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-COOH} \xrightarrow[Pd,BaSO_4]{H_2}$$

$$\rightarrow \underset{(IV)}{CH_3-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-COOH} \xrightarrow{SOCl_2} CH_3-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-COCl \xrightarrow{NH_3}$$

$$\rightarrow \underset{(V)}{CH_3-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CONH_2}$$

Based on its complete analysis the crystalline condensation product is an isomer of nitrile (II). When nitrile (II), containing the crystalline nitrile as impurity, was saponified, the crystalline product was recovered unchanged. From this it was concluded that it is saponified with greater difficulty. For this reason the hydrolysis of the crystalline nitrile was run with a larger amount of mixed hydrochloric and acetic acids, and for a longer time. Under these conditions both the chlorine and cyanide groups were saponified and the hydrolysis product proved to be phenylsuccinic acid.



$$CCl_2{=}\underset{\displaystyle C_6H_5}{\underset{|}{C}}-CH_2-CN \xrightarrow[CH_3COOH]{HCl} HOOC-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-CH_2-COOH$$

The formation of phenylsuccinic acid indicates that the crystalline nitrile differs from the α-isomer only in the position of the phenyl group, and consequently is β-phenyldichlorovinylacetonitrile (I). To prove conclusively the structure of (I) we are synthesizing it by a counter method.

EXPERIMENTAL

The condensation of γ,γ,γ-trichlorocrotononitrile with benzene was run in the same manner as described earlier [1]. The results are summarized in the table.

Expt. no.	Relative amounts of reactants (g-mole)*		Temperature	Reaction time (in hrs)		Yields of products (in % of theoretical)	
	$AlCl_3$	C_6H_6		heating	standing at 20°	liquid nitrile (II)	crystalline nitrile (I)
1	1.17	25.7	45°	5	12	27	Not isolated
2	1.80	25.7	20		22	24	Traces
3	1.00	10.0	60–70	10.5	12	43	Not isolated
4	0.94	13.6	60–70	12.5	36	31	9.6
5	0.80	13.6	60–75	15	84	11.5	11.5
6	1.20	10.0	65–70	6	12	44.3	9.7
7	1.20	10.0	70	2	—	62	Not isolated

α-Phenyldichlorovinylacetonitrile (II):

B. p. 122° at 3 mm, 125-127° at 5 mm, 140-145° at 8 mm, $n^{20}D$ 1.5585, d_4^{20} 1.2553, MR_D 54.48; calc. 53.86.

The analysis results for (II) and its complete saponification to phenylsuccinic acid were presented earlier [1].

α-Phenyldichlorovinylacetic acid (III). A mixture of 7.75 g of nitrile (II), 9 ml of concentrated hydrochloric acid, 16 ml of glacial acetic acid and 4 ml of water was refluxed for 17 hrs, and then allowed to stand at room temperature for 48 hrs. When the mixture was cooled the top brownish layer solidified, while the aqueous layer deposited white crystals. We obtained 7.5 g of crude product.

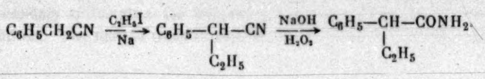
To isolate the pure acid a benzene solution of the saponification product was chromatographed through a column containing Al_2O_3. All of the colored impurities were eluted with benzene until the Al_2O_3 layer became white. The aluminum oxide with tenaciously adsorbed acid was pushed out of the column and then treated several times with 10% $NaHCO_3$ solution until all of the acid had been extracted. Acidification of the alkaline solution gave the nearly pure acid with m. p. 83-86°. After recrystallization from either cyclohexane or petroleum ether, m. p. 88-89°. From the literature, m. p. 87-88° [4].

Two substances were isolated from the benzene solution used to elute the column. One of them was orange in color, had m. p. 196-198° (from benzene), and was insoluble in ether and dilute NaOH solution. It contained both halogen and nitrogen.

The second substance with m. p. 90-91.5° proved to be nitrile (I). Its mixed melting point with nitrile (I), isolated from the condensation product, was not depressed.

α-Phenylbutyric acid (IV). A solution of 2 g of acid (III) in 30 ml of water containing 1.4 g of NaOH was hydrogenated over $Pd/BaSO_4$ at room temperature. Here 625 ml of H_2 was absorbed. At the end of hydrogenation the catalyst was suction-filtered, and the alkaline solution after evaporation was acidified. The acid was extracted with ether, dried, and vacuum-distilled. We obtained 1.1 g of acid (IV) with b. p. 160-170° (6 mm).

α-Phenylbutyramide (V). A mixture of 1.1 g of acid (IV) and 5 ml of $SOCl_2$ was refluxed for an hour. After distilling off the excess $SOCl_2$ in vacuo the crude chloride was converted to the amide by treatment with 25% ammonia solution. We obtained 0.6 g of amide (V) with m. p. 83-84.5° (from benzene), which failed to depress the melting point when mixed with the α-phenylbutyramide obtained by us from benzyl cyanide by the scheme



$$C_6H_5CH_2CN \xrightarrow[Na]{C_2H_5I} C_6H_5-\underset{\displaystyle C_2H_5}{\underset{|}{CH}}-CN \xrightarrow[H_2O_2]{NaOH} C_6H_5-\underset{\displaystyle C_2H_5}{\underset{|}{CH}}-CONH_2$$

The ethylation of benzyl cyanide was run by the Wegler method [5]. To saponify the nitrile we used the method repeatedly employed by us earlier [1].

β-Phenyldichlorovinylacetonitrile (I). The product, isolated from several condensations (Table, Nos. 4-6), represents a single substance, crystallizing from benzene as coarse, colorless, well-shaped crystals with m. p. 92-92.5°. It is insoluble in petroleum ether, moderately soluble in diethyl ether, and has a sharp odor reminiscent of chlorine.

Found %: C 56.83; H 3.34; Cl 34.02; N 6.88. $C_{10}H_7NCl_2$. Calculated %: C 56.60; H 3.30; Cl 33.49; N 6.60.

Saponification of nitrile (I). A mixture of 1 g of nitrile (I), 4 ml of glacial acetic acid, 2 ml of concentrated HCl and 0.5 ml of water was refluxed with mechanical stirring for 13 hrs (and then allowed to stand at room temperature for 60 hrs). On pouring into water a brown oil separated that solidified on standing. The obtained substance proved to be insoluble in 10% soda solution, while the residue from the evaporation of the acid solution yielded only a trace amount of acid, which could not be purified.

The substance was again dissolved in 10 ml of CH_3COOH and refluxed with 8 ml of HCl for 19 hrs (the mixture was allowed to stand for 96 hrs). A small amount of the water-insoluble substance was removed and washed with 10% soda solution. No indication of solution was observed here. The acid solution was carefully evaporated on the water bath to a small volume. On cooling a precipitate of phenylsuccinic acid was obtained, which was reprecipitated from soda solution. We obtained 0.2 g of the acid. M. P. 164-165° (from a mixture of benzene and anhydrous alcohol). The mixed melting point with authentic phenylsuccinic acid was not depressed.

SUMMARY

1. γ,γ,γ-Trichlorocrotononitrile adds benzene at the double bond in the presence of 0.8-0.9 g-mole of $AlCl_3$, which indicates its high activity.

2. The reaction product is a mixture of α-phenyldichlorovinylacetonitrile and, apparently, β-phenyldichlorovinylacetonitrile. The relative amount of the two isomers in the mixture depends on the reaction conditions.

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CATALYTIC AMINATION OF ORGANIC COMPOUNDS

VII. CATALYTIC TRANSFORMATIONS IN THE BUTYLAMINE SERIES

N. S. Kozlov and N. I. Panova

In studying the catalytic amination of alcohols and of aliphatic ethers and esters [1-3] it was established by us that in all cases the end reaction products are a mixture of the corresponding primary, secondary and tertiary amines. Consequently, in order to elucidate the mechanism of the amination reactions taking place here the need arose to investigate the behavior shown by various individual amines under our studied conditions.

Some light on this problem was found in the patent literature. Thus, it is known that the passage of a mixture of butylamine and ammonia over aluminum oxide heated to 350° gave a catalyzate that contained 60% of unchanged butylamine, 34% of dibutylamine, 3% of butylene and 3% of other products [4]. If the aluminum oxide had been previously treated with acid, then here the yield of secondary amine showed a slight increase [5, 6].

A paper was recently published by A. F. Plate and co-workers [7], in which experiments on the conversion of propylamine to a mixture of primary, secondary and tertiary amines by passage over aluminomolybdenum catalyst are described.

In the present paper we studied the catalytic transformations of butylamine, dibutylamine and tributylamine when passed in a stream of compressed ammonia over heated aluminum oxide. Here it was established that any of the indicated starting amines give butylene and two new amines: the primary amine gives the secondary and tertiary amines, the secondary amine gives the primary, and tertiary amines and the tertiary amine gives the primary and secondary amines. The mutual transformations of the amines can be depicted by the following general equation:

$$6C_4H_9NH_2 \rightleftarrows 3(C_4H_9)_2NH + 3NH_3 \rightleftarrows 2(C_4H_9)_3N + 4NH_3$$

Consequently, the experimental data obtained by us indicate that the mutual transformations of the butylamines bear an equilibrium character, in which connection the equilibrium is shifted strongly toward the formation of the primary amine.

The formation of butylene in these reactions can occur as the result of the following chemical processes:

$$C_4H_9NH_2 = C_4H_8 + NH_3,$$
$$(C_4H_9)_2NH = C_4H_8 + C_4H_9NH_2,$$
$$(C_4H_9)_3N = C_4H_8 + (C_4H_9)_2NH.$$

At the present time we lack experimental data showing that butylene participates in the formation of the amines. However, using compressed ammonia, we were largely able to suppress the conversion of the primary butylamine to butylene. We also made an attempt to study the reverse reaction, where as the starting ethylenic hydrocarbon we took amylene with b. p. 33°, obtained by the dehydration of isoamyl alcohol. From 10 ml of amylene taken for reaction we obtained several drops of the amine. Using the micro technique it was shown that the obtained amine has a primary character and distills completely up to 150°.

Such a reaction character is probably explained as follows: here, apparently, ammonia adds to the double bond in accord with the V. V. Markovnikov rule, in which case a primary amine is formed with the amino group on the secondary carbon atom. But amines having such a structure, as was shown in our previous paper [2], are extremely unstable.

EXPERIMENTAL

The experiments were run in the same apparatus used by us earlier [1]. A known weight of starting amine in an atmosphere of ammonia under a pressure of 9 atmos, was passed at a rate of 20 drops per min over aluminum oxide heated to 370-375°. The amines taken for experiment had the following constants: n-butylamine, b. p. 77-79°, d_4^{20} 0.743, $n^{20}D$ 1.403; di-n-butylamine, b. p. 158-160°, d_4^{20} 0.767, $n^{20}D$ 1.423; and tri-n-butylamine, b. p. 214-218°, d_4^{20} 0.774, $n^{20}D$ 1.425.

The gaseous reaction product proved to be butylene, which was determined by the method described in the previous paper [2]. The liquid catalyzate, boiling in the range 75-180° independent of the amine taken was a mixture of primary, secondary and tertiary amines, and did not contain any neutral products. The catalyzate was analyzed by the method given in [8].

The results of our experiments are summarized in the table.

Name of compound	Am't of compound (in g)	Ammonia pressure (atmos)	Yield of catalyzate (in g)	Properties of catalyzate		Am't of amines in catalyzate			Am't, of butylene (in liters)
				primary	secondary	primary	secondary	tertiary	
n-Butylamine	30	9	25	0.743	1.408	52.6	32.3	15.1	2
Dibutylamine	30	9	22	0.771	1.411	57.0	20.5	22.5	3
Tributylamine	13	9	9	0.763	1.416	52.8	22.2	25.0	1
n-Butylamine	10	1	4	—	—	—	—	—	4

SUMMARY

The mutual transformations of butyl-, dibutyl- and tributylamine over aluminum oxide in an ammonia atmosphere under variable pressure were studied. Compressed ammonia shifts the equilibrium toward the formation of the primary amine and suppresses the formation of the unsaturated hydrocarbon.

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PROPERTIES OF BINARY MIXTURES OF ORGANIC COMPOUNDS AS A FUNCTION OF ASSOCIATION AND CONCENTRATION

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The dependence of various physical properties of mixtures on the concentration and especially the extent of their deviation from additivity are extensively used to study intermolecular reaction and association of molecules in solution, either between themselves or with the molecules of the solvent [1]. Here it is postulated that a negative deviation of the viscosity and density of a mixture from additivity [2] or deviation from a linear change in the molar polarization of a dissolved substance, calculated from the dielectric permeability, is a sign that the molecules of the components show association [1]. On this basis it is frequently postulated that the molecules of many substances (chlorobenzene, benzonitrile, etc.), for which other criteria and properties suggest a normal behavior [4], are capable of association [3]. In order to ascertain more accurately the effect of molecular association of the components on the character of the concentration dependence of various physical properties of binary mixtures, we measured the values of one of the equilibrium (density $d_{1,2}$), kinetic (viscosity $\eta_{1,2}$) and electrical (dielectric permeability $\epsilon_{1,2}$) properties of sundry binary mixtures, composed of a constant component 1 (benzene), while as component 2 we took various compounds whose molecules differed mainly only in the dipole moment (isoperiodic compounds), mass (isologs), or in all the properties except shape (monosubstituted benzenes). The methods used to make the measurements and to purify the compounds are given in the dissertation by one of the authors [5]; the measurement results obtained for 25 mixtures of the indicated type are given in Tables 1-10, and for some concentrations and temperatures were presented earlier [6]. The dissertation [5] also has a number of curves, constructed from the data obtained for the relationship between the concentration N_2 (in mole fractions) and the described properties, and also the calculated deviations of the latter from additivity using the equation

$$\Delta y = y_{1,2} - [N_2 y_2 + (1 - N_2) y_1]$$

where

$$y = d, \eta, v \text{ or } \epsilon.$$

From the obtained data it follows that contraction of the system occurs when benzene is mixed with its monohalo derivatives, which is confirmed by the measurement results obtained by other authors [3, 7]. The same is also true for mixtures of benzene with bromo- and iodobutane. Only for the mixture benzene-chlorobutane is the $d_{1,2}$-N_2 curve somewhat convex to the N_2 axis. The $\Delta v_{1,2}$-N_2 curves ($\Delta v_{1,2}$ is the deviation of the specific volume of the mixture from additivity) pass through a minimum, in which connection the maximum relative decrease in the volume on mixing increases with the mass of the halogen.

In the case of mixtures of benzene with aromatic isoperiodic compounds a contraction of the system is observed for both normal (except the mixture benzene-ethylbenzene) and associated mixtures, while, on the other hand, an expansion of the system is observed for mixtures of benzene with aliphatic isoperiodic compounds (except the mixture containing ethyl methyl ketone). A similar type of difference in the behavior of the discussed mixtures also follows from the literature data for $d_{1,2}$ [3, 8].

The mixtures with associated components also do not differ from the mixtures with normal (nondissociated) compounds in respect to the character of the change in $\Delta v_{1,2}$ with N_2 and $d_{1,2}$ with the temperature. The $\Delta v_{1,2}$-N_2

TABLE 1

Dielectric Permeability $\epsilon_{1,2}$ of Binary Mixtures Composed of Benzene (1) and Halogenated Derivatives (2)

Component 2	N_2	ε^{25}	ε^{50}	$\Delta\varepsilon \cdot 10^2$ at 25°	Component 2	N_2	ε^{25}	ε^{50}	$\Delta\varepsilon \cdot 10^2$ at 25°
C_6H_5Cl	0.040	2.41	—	+1	n-C_4H_9 Cl	0.048	2.54	—	+3
	0.080	2.60	—	+6		0.098	2.80	—	+4
	0.121	2.76	—	+9		0.153	3.06	—	+3
	0.162	2.89	—	+9		0.2	3.35	3.12	+8
	0.2	3.00	2.87	+6		0.5	4.76	4.42	−2
	0.5	4.02	3.81	+8		0.8	6.22	5.71	−7
	0.8	4.95	4.64	+1		1.0	7.29	6.54	—
	1.0	5.61	5.23	—		0.0	2.27	2.24	—
C_6H_5Br	0.028	2.38	—	+2	n-C_4H_9Br	0.033	2.48	—	+6
	0.057	2.52	—	+7		0.66	2.66	—	+8
	0.086	2.60	—	+6		0.100	2.86	—	+12
	0.116	2.72	—	+9		0.134	3.04	—	+14
	0.2	3.01	2.88	+11		0.2	3.32	3.16	+11
	0.5	3.97	3.77	+13		0.5	4.77	4.42	+10
	0.8	4.86	4.57	+9		0.8	6.09	5.59	+7
	1.0	5.40	5.08	—		1.0	6.96	6.34	—
C_6H_5I	0.022	2.34	—	+2					
	0.044	2.40	—	+3					
	0.066	2.50	—	+7					
	0.089	2.56	—	+8					
	0.2	2.88	2.77	+13					
	0.5	3.67	3.54	+19					
	0.8	4.37	4.17	+16					
	1.0	4.69	4.49	—					

curves for many of the studied mixtures, especially the mixtures of benzene with isoperiodic compounds (including associated mixtures), within the limits of experimental error, obey the Biron rule [7, 9]: $\Delta v_{1,2} = KN_2(1 - N_2)$ (K is constant at a given temperature). The density of all of the studied mixtures decreases linearly with increase in the temperature in the studied temperature interval, while the value $\Delta v_{1,2}$, in the case of a negative sign, increases with increase in the temperature, and, to the contrary, decreases if the sign is positive. Only for mixtures with associated compounds and with a positive sign for $\Delta v_{1,2}$ does the value of the latter increase with the temperature.

All of the investigated mixtures failed to show a linear change of $\epsilon_{1,2}$ with N_2. In harmony with the results of other measurements [3, 10], even the mixtures benzene-chlorobenzene, benzene-ethylbenzene and benzene-diethyl ether, considered to be either ideal or nearly ideal [11], show a noticeable and uniform change in $\Delta\epsilon_{1,2}$ with N_2. In this connection, at the same concentrations N_2 and temperatures, those mixtures whose members belong to the same series of halo derivatives show a consistent change in $\Delta\epsilon_{1,2}$ with increase in the mass of the halogen.

Mixtures of benzene with the studied aromatic compounds, except benzyl alcohol, o-cresol and aniline, give a positive $\Delta\epsilon_{1,2}$. Mixtures of benzene with the studied aliphatic isoperiodic compounds give $\Delta\epsilon_{1,2}$-N_2 curves that are always convex to the N_2 axis (negative $\Delta\epsilon_{1,2}$). Here only a larger $|\Delta\epsilon_{1,2}|$ is characteristic for mixtures of benzene with compounds tending to form complexes due to hydrogen bonding between the molecules (propionic acid, butanol). Evidently, the fact that a mixture has a negative deviation of $\epsilon_{1,2}$ from additivity is not a good criterion that the molecules of the components in the mixture show association. This is due to the fact that differences in the other properties of the component molecules, such as the dipole moment, polarizability and shape [4, 6], also exert an influence on the sign and value of $\Delta\epsilon_{1,2}$. It should also be mentioned that but for a few exceptions the sign of $\Delta\epsilon_{1,2}$ coincides with that for $\Delta d_{1,2}$. Apparently, $\Delta\epsilon_{1,2}$ is associated with the number of component molecules per unit volume of mixture that deviate from additivity.

Within the limits of measurement error, the $\Delta\epsilon_{1,2}$-N_2 curves for nearly all of the studied mixtures (including the mixtures with associated components) are quite symmetrical, and the value $\Delta\epsilon_{1,2}$ is satisfactorily calculated using the equation: $\Delta\epsilon_{1,2} = K'N_2(1 - N_2)$ (K' is a constant). The mixtures with associated components (alcohols,

TABLE 2

Dielectric Permeability $\epsilon_{1,2}$ of Binary Mixtures Composed of Benzene (1) and Members of Aromatic Isoperiodic Series (2)

Component 2	N_2	ε^{25}	ε^{35}	ε^{45}	ε^{55}	$\Delta\varepsilon \cdot 10^2$ at 25°
$C_6H_5C_2H_5$	0.1	2.28	2.25	2.22	2.20	0
	0.2	2.30	2.28	2.26	2.24	0
	0.4	2.31	2.29	2.27	2.25	−1
	0.5	2.33	2.30	2.28	2.26	−1
	0.6	2.34	2.32	2.30	2.29	−1
	0.8	2.36	2.34	2.38	2.30	−2
	1.0	2.41	—	—	—	—
$C_6H_5OCH_3$	0.1	2.49	2.46	2.42	2.38	+1
	0.2	2.72	2.67	2.64	2.60	+3
	0.4	3.16	3.10	3.06	3.01	+6
	0.5	3.40	3.32	3.27	3.22	+9
	0.6	3.63	3.54	3.48	3.42	+11
	0.8	4.01	3.93	3.83	3.77	+8
	1.0	4.35	—	—	—	—
$C_6H_5CH_2OH$	0.1	2.77	2.74	2.70	2.66	—
	0.2	3.40	3.34	3.27	3.22	—
	0.5	6.25	5.94	5.68	5.42	—
$C_6H_4(CH_3)OH$-*o*	0.1	2.64	2.60	2.55	2.51	−10
	0.2	3.04	2.99	2.93	2.88	−17
	0.4	3.91	3.31	3.71	3.60	−24
	0.5	4.36	4.25	4.12	4.00	−28
	0.6	4.87	4.70	7.54	4.41	−22
	0.8	5.96	5.72	5.50	5.25	−7
	1.0	6.97	—	—	—	—
C_6H_5CN	0.2	6.98	6.72	6.50	6.34	—

TABLE 3

Dielectric Permeability $\epsilon_{1,2}$ of Binary Mixtures Composed of Benzene (1) and Members of Aliphatic Isoperiodic Series (2)

Component 2	N_1	ε^{20}	ε^{30}	ε^{40}	ε^{50}	$\Delta\varepsilon \cdot 10^2$ at 25°
$(C_2H_5)_2NH$	0.2	2.58	2.51	—	—	−3
	0.4	2.88	2.81	—	—	−7
	0.5	3.04	2.95	—	—	−8
	0.6	3.22	3.10	—	—	−7
	0.8	3.56	3.41	—	—	−6
	1.0	3.96	—	—	—	—
$(C_2H_5)_2O$	0.2	2.66	—	—	—	−4
	0.4	3.06	—	—	—	−4
	0.5	3.28	—	—	—	−4
	0.6	3.48	—	—	—	−5
	0.8	3.91	—	—	—	−4
	1.0	4.265 (25°)	—	—	—	—
CH_3COOCH_3	0.5	4.82	4.66	—	—	—
	1.0	7.3	—	—	—	—

TABLE 3 (continued)

Component 2	N_2	ε^{20}	ε^{30}	ε^{40}	ε^{50}	$\Delta\varepsilon \cdot 10^3$ at 25°
$HCOOC_2H_5$	0.2	3.33	3.26	—	—	−17
	0.4	4.49	4.36	—	—	—
	0.5	5.11	4.97	—	—	—
	1.0	8.4	—	—	—	—
C_2H_5COOH	0.2	2.36	2.34	2.32	2.30	−10
	0.4	2.49	2.48	2.47	2.46	−15
	0.5	2.66	2.56	2.55	2.55	−17
	0.8	2.92	2.93	2.96	2.96	−8
	1.0	3.19	—	—	—	—
n-C_4H_9OH	0.2	3.46	3.35	3.25	3.19	~−192
	0.4	8.03	7.40	6.71	6.08	—
	1.0	17.8 [13]				
$CH_3COC_2H_5$	0.2	4.64	4.49	4.37	4.24	~−78
	1.0	18.0 [13]				

TABLE 4

Dielectric Permeability $\epsilon_{1,2}$ and Deviations from Additivity $\Delta\epsilon_{1,2}$ of Mixtures of Benzene (1) with Its Derivatives (2)

Component 2	N_2	ε^{25}	ε^{55}	$\Delta\varepsilon^{25}$
$C_6H_5OC_2H_5$	0.2	2.81	2.69	−0.13
	0.5	3.48	3.30	+0.18
	1.0	4.35	4.07	—
$C_6H_5N(CH_3)_2$	0.2	3.03	2.88	+0.21
	0.5	3.94	3.71	+0.28
	1.0	5.05	4.70	—
$C_6H_5NH_2$	0.2	3.09	2.94	−0.13
	0.5	4.44	4.12	−0.22
	1.0	7.07	6.34	—
$C_6H_5CH_2Cl$	0.2	3.31	3.16	+0.15
	0.5	4.72	4.48	+0.17
	1.0	6.85	6.34	—
$C_6H_5COOC_2H_5$	0.2	3.32	3.13	+0.30
	0.5	4.56	4.25	+0.40
	1.0	6.06	5.56	—
C_6H_5CHO	0.1	3.62	3.40	~−0.22
	0.2	5.02	4.64	~−0.49
	1.0	18.0 [13]		
$C_6H_5NO_2$	0.2	—	6.50	—
C_6H_5OH	0.2	3.40	3.11	—
	0.5	6.10	5.14	—

TABLE 5

Density of Mixtures of C_6H_6 (1) and Halo Derivatives at Various Temperatures

Component 2	N_2	d^{25}	d^{35}	d^{45}	d^{50}	$\Delta v \cdot 10^4$	
						25°	50°
n-C_4H_9Cl	0.000	0.8734	0.8628	0.8721	0.8468	—	—
	0.098	0.8736	0.8629	0.8522	0.8466	+4	+4
	0.153	0.8737	0.8630	0.8523	0.8468	1	5
	0.800	0.8773	—	—	0.8793	6	0
	1.000	0.8787	0.8675	0.8561	0.8504	—	—
n-C_4H_9Br	0.066	0.9038	0.8929	0.8821	0.8767	—58	—65
	0.100	0.9191	0.9080	0.8970	0.8915	—80	—86
	0.134	0.9344	0.9232	0.9120	0.9064	—101	—107
	0.800	1.1972	—	—	1.1623	—73	—77
	1.000	1.2638	1.2493	1.2348	1.2275	—	—
n-C_4H_9I	0.075	0.9404	0.9292	0.9179	0.9123	—143	—150
	0.100	0.9629	0.9575	0.9411	0.9344	—186	—195
	0.800	1.4784	—	—	1.4387	—118	—120
	1.000	1.5989	1.5823	1.5658	1.5575	—	—
C_6H_5Cl	0.080	0.8941	0.8833	0.8724	0.8669	—31	—27
	0.121	0.9044	0.8936	0.8828	0.8775	—45	—46
	0.162	0.9147	0.9039	0.8932	0.8879	—53	—55
	0.800	1.0602	—	—	1.0329	—42	—42
	1.000	1.1010	1.0902	1.0793	1.0739	—	—
C_6H_5Br	0.0867	0.9355	0.9244	0.9133	0.9078	—102	—102
	0.116	0.9565	0.9452	0.9340	0.9283	—130	—129
	0.800	1.3811	—	—	1.3483	—83	—86
	1.000	1.4885	1.4752	1.4616	1.4543	—	—
C_6H_5I	0.0668	0.9512	0.9401	0.9291	0.9235	—166	—173
	0.0896	0.9774	0.9661	0.9549	0.9492	—208	—215
	0.800	1.6596	—	—	1.6235	—118	—121
	1.000	1.8163	1.8013	1.7862	1.7782	—	—

TABLE 6

Density of Mixtures of C_6H_6 (1) and Members of the Same Aromatic Isoperiodic Series (2) at Various Temperatures

Component 2	N_2	d^{25}	d^{35}	d^{45}	d^{50}	$\Delta v \cdot 10^4$	
						25°	50°
$C_6H_5C_2H_5$	0.1	0.8715	0.8610	0.8506	0.8454	+10	+ 8
	0.2	0.8698	0.8595	0.8494	0.8443	+18	+15
	0.4	0.8672	0.8574	0.8475	0.8427	+24	+20
	0.5	0.8660	0.8565	0.8470	0.8422	+24	+17
	0.6	0.8650	0.8557	0.8464	0.8417	+24	+17
	0.8	0.8635	0.8545	0.8454	0.8410	+15	+ 9
	1.0	0.8624	0.8536	0.8448	0.8404	—	—
$C_6H_5OCH_3$	0.1	0.8874	0.8768	0.8662	0.8610	—31	—34
	0.2	0.9007	0.8904	0.8801	0.8750	—51	—60
	0.4	0.9256	0.9156	0.9056	0.9007	—69	—81
	0.5	0.9373	0.9273	0.9175	0.9126	—69	—79
	0.6	0.9485	0.9386	0.9289	0.9240	—63	—71
	0.8	0.9696	0.9600	0.9504	0.9456	—39	—43
	1.0	0.9891	0.9797	0.9703	0.9656	—	—

TABLE 6 (continued)

Component 2	N_2	d^{25}	d^{35}	d^{45}	d^{50}	$\Delta v \cdot 10^4$	
						25°	50°
$C_6H_5CH_2OH$	0.1	0.8932	0.8827	0.8722	0.8670	−40	−40
	0.2	0.9122	0.9021	0.8920	0.8870	−67	−7[illegible]
	0.5	0.9651	0.9561	0.9470	0.9426	−91	−100
	0.8	1.0122	1.0039	0.9957	0.9915	−53	−60
	1.0	1.0401	1.0322	1.0244	1.0206	—	—
C_6H_5CHO	0.1	0.8926	0.8822	0.8718	0.8665	−35	−45
	0.2	0.9115	0.9012	0.8912	0.8861	−59	−71
	0.4	0.9472	0.9374	0.9278	0.8230	−77	−92
	0.5	0.9642	0.9548	0.9454	0.9407	−77	−93
	0.6	0.9806	0.9713	0.9621	0.9575	−72	−87
	0.8	1.0119	1.0029	0.9940	0.9896	−41	−52
	1.0	1.0421	1.0332	1.0243	1.0199	—	—
C_6H_5CN	1.0	1.0408	1.0321	1.0233	1.0189		
	0.2	0.9031	0.8930	0.8830	0.8780	−53	−66

TABLE 7

Density of Mixtures of C_6H_6 (1) and Members of the Same Aliphatic Isoperiodic Series (2) at Various Temperatures

Component 2	N_2	d^{20}	d^{30}	d^{35}	d^{45}	$\Delta v \cdot 10^4$	
						20°	35°
$(C_2H_5)_2NH$	0.2	0.8391	0.8285	0.8232	—	+70	+68
	0.4	0.8022	0.7917	0.7865	—	+110	+104
	0.5	0.7847	0.7743	0.7691	—	+117	+109
	0.6	0.7686	0.7582	0.7529	—	+100	+91
	0.8	0.7356	0.7250	0.7197	—	+78	+70
	1.0	0.7051	0.6943	0.6885	—	—	—
$(C_2H_5)_2O$	0.2	0.8440	—	—	—	+25	—
	0.4	0.8105	—	—	—	+33	—
	0.5	0.7941	—	—	—	+35	—
	0.6	0.7778	—	—	—	+33	—
	0.8	0.7457	—	—	—	+20	—
	1.0	0.7138	—	—	—	—	—
C_2H_5COOH	0.2	0.8961	0.8854	0.8800	0.8699	+69	+71
	0.4	0.9159	0.9051	0.8997	0.8889	+103	+106
	0.5	0.9269	0.9160	0.9106	0.8998	+106	+110
	0.8	0.9640	0.9531	0.9477	0.9368	+69	+71
	1.0	0.9934	0.9824	0.9770	0.9661	—	—
n-C_4H_9OH	0.2	0.8630	0.8526	0.8474	0.8370	+25	+32
	0.4	0.8489	0.8390	0.8341	0.8243	+30	+37
	0.5	0.8421	0.8326	0.8279	0.8184	+29	+34
	0.6	0.8356	0.8264	0.8210	0.8126	+23	+28
	0.8	0.8226	0.8141	0.8098	0.8014	+10	+14
	1.0	0.8095	0.8017	0.7978	0.7900	—	—
CH_3COOCH_3	0.5	0.9004	0.8887	0.8829	—	+64	+59
	1.0	0.9325	0.9191	0.9124	—	—	—
$HCOOC_2H_5$	0.2	0.8832	0.8721	0.8665	—	+29	+29
	0.4	0.8889	0.8774	0.8716	—	+43	+42
	0.5	0.8920	0.8804	0.8745	—	+46	+43
	0.8	0.9036	0.8910	0.8849	—	+26	+29
	1.0	0.9125	0.8955	0.8931	—	—	—
$CH_3COC_2H_5$	0.2	0.8646	0.8538	0.8485	0.8378	−6	−7
	0.4	0.8502	0.8395	0.8343	0.8237	−10	−13
	0.5	0.8430	0.8324	0.8271	0.8166	−12	−15
	0.6	0.8357	0.8251	0.8198	0.8092	−13	−15
	0.8	0.8201	0.8094	0.8041	0.7935	0	0
	1.0	0.8055	0.7948	0.7895	0.7789	—	—

TABLE 8

Viscosity $\eta_{1,2} \cdot 10^5$ of Mixtures of Benzene and Halo Derivatives (Isologs) at Various Temperatures

Halo derivative (2)	N_2	η^{25}	η^{35}	η^{45}	η^{50}	$\Delta\eta \cdot 10^3$	
						25°	50°
$n\text{-}C_4H_9Cl$	0.000	602	527	464	436	—	—
	0.098	557	492	437	417	−0.28	−0.09
	0.153	542	481	428	404	−0.33	−0.17
	0.800	454	—	—	358	−0.25	−0.12
	1.000	428	390	356	340	—	—
$n\text{-}C_4H_9Br$	0.066	588	518	459	432	−0.14	−0.06
	0.100	583	515	457	431	−0.19	−0.09
	0.134	574	510	454	428	−0.16	−0.10
	1.000	606	552	502	476	—	—
C_6H_5Cl	0.080	613	537	475	444	−0.02	−0.01
	0.121	620	544	482	451	0.0	−0.01
	0.162	623	547	486	454	−0.03	−0.02
	0.800	718	—	—	541	−0.06	−0.02
	1.000	750	669	601	566	—	—
C_6H_5Br	0.0867	636	558	492	461	−0.05	−0.05
	0.116	649	568	504	470	−0.07	−0.07
	0.800	960	—	—	711	−0.07	−0.02
	1.000	1056	934	836	784	—	—
C_6H_5I	0.0668	646	565	499	469	−0.16	−0.10
	0.0896	660	578	512	478	−0.22	−0.15
	0.800	1274	—	—	917	−0.33	−0.16
	1.000	1513	1318	1162	1083	—	—

TABLE 9

Viscosity $\eta_{1,2} \cdot 10^5$ of Mixtures of Benzene (1) and Members of Aromatic Series of Isoperiodic Compounds (2) at Various Temperatures

Component 2	N_2	η^{25}	η^{35}	η^{45}	η^{50}	$\Delta\eta \cdot 10^5$	
						25°	50°
$C_6H_5C_2H_5$	0.1	599	528	468	440	−5	0
	0.2	601	530	471	443	−6	−1
	0.4	603	535	477	449	−8	−2
	0.5	607	538	481	453	−7	−2
	0.6	608	542	484	456	−8	−3
	0.8	616	551	492	466	−4	0
	1.0	625	560	502	474	—	—
$C_6H_5OCH_3$	0.1	635	556	489	460	−5	−1
	0.2	671	587	517	485	−8	−2
	0.4	742	649	570	533	−14	−4
	0.5	782	680	597	559	−12	−4
	0.6	821	715	626	585	−11	−3
	0.8	907	785	684	640	−2	+1
	1.0	986	851	739	690	—	—
$o\text{-}C_6H_4(CH_3)OH$	0.1	704	609	531	497	−587	−178
	0.2	849	727	623	578	−1131	−337
	0.4	1319	1073	894	815	−2039	−572
	0.5	1661	1334	1084	981	−2386	−652
	0.6	2148	1668	1331	1186	−2589	−586
	0.8	3874	2766	2067	1807	−2241	−544
	1.0	7493	4853	3359	2830	—	—

TABLE 9 (continued)

Component 2	N_2	η^{25}	η^{35}	η^{45}	η^{50}	$\Delta\eta\cdot10^5$	
						25°	50°
$C_6H_5CH_2OH$	0.1	700	597	526	493	−369	−158
	0.2	855	714	617	575	−682	−292
	0.5	1712	1379	1139	1026	−1227	−487
	0.8	3267	2433	1904	1695	−1074	−467
	1.0	5276	3891	2945	2591	—	—
C_6H_5CHO	0.1	655	583	509	477	−28	−13
	0.2	714	625	551	517	−50	−27
	0.4	847	742	667	—	−79	—
	0.5	928	809	711	665	−78	−42
	0.6	1012	885	773	724	−56	−22
	1.0	1411	1215	1051	975	—	—
C_6H_5CN	0.2	688	605	532	498	−43	−24
	1.0	1249	1071	931	866	—	—

TABLE 10

Viscosity $\eta_{1,2}\cdot10^5$ of Mixtures of Benzene (I) and Members of Aliphatic Series of Isoperiodic Compounds (2) at Various Temperatures

Component 2	N_2	η^{20}	η^{30}	η^{35}	η^{45}	$\Delta\eta\cdot10^5$	
						20°	35°
$(C_2H_5)_2NH$	0.2	522	463	438	—	−60	−38
	0.4	440	393	374	—	−76	−52
	0.5	411	367	350	—	−73	−51
	0.6	387	348	333	—	−64	−42
	0.8	349	314	298	—	−36	−27
	1.0	320	288	274	—	—	—
$(C_2H_5)_2O$	0.2	504	—	—	—	−14	—
	0.4	407	—	—	—	−81	—
	0.5	371	—	—	—	−77	—
	0.6	339	—	—	—	−70	—
	0.8	289	—	—	—	−40	—
	1.0	250	—	—	—	—	—
C_2H_5COOH	0.2	660	575	542	480	−78	−58
	0.4	700	610	575	510	−129	−99
	0.5	734	639	602	533	−140	−108
	0.8	889	774	729	643	−121	−92
	1.0	1101	944	894	783	—	—
$n\text{-}C_4H_9OH$	0.2	714	604	562	490	−387	−254
	0.4	898	746	687	584	−657	−419
	0.5	1054	864	791	662	−727	−459
	0.6	1279	1021	924	761	−729	−471
	0.8	1920	1490	1335	1062	−542	−350
	1.0	2916	2253	1974	1539	—	—
CH_3COOCH_3	0.5	480	428	406	—	—	−34
	1.0	411	372	354	—	—	—
$HCOOC_2H_5$	0.2	558	491	465	—	−43	−29
	0.4	501	446	427	—	−54	−34
	0.5	482	430	409	—	−50	−35
	0.8	435	391	373	—	−29	−21
	1.0	418	378	361	—	—	—
$CH_3COC_2H_5$	0.2	569	498	471	421	−31	−21
	0.4	511	454	431	388	−41	−27
	0.5	487	434	414	373	−42	−27
	0.6	471	420	401	362	−34	−22
	0.8	435	391	373	339	−23	−16
	1.0	411	370	355	322	—	—

acids, amines) show only much higher values of the constant K'. In the temperature range studied all of the mixtures show a decrease in $\epsilon_{1,2}$ with increase in the temperature [3, 12]. A characteristic of the mixtures with the indicated associated compounds is either an abnormally low (for the acids) or, to the contrary, a high (for the alcohols and phenols) value of $\Delta\epsilon/\Delta t$.

The data for the viscosities of the studied mixtures also do not show any qualitative difference in the character of the relationship between $\eta_{1,2}$ and N_2 for the mixtures with associated and nonassociated components. The $\eta_{1,2}$-N_2 curves for all the mixtures, including those with acids, alcohols and phenols as the 2 components, are characterized by a negative deviation of $\eta_{1,2}$ from additivity. Here many highly polar members of the isoperiodic series give mixtures with benzene that are characterized by extremely high absolute values of $\Delta\eta_{1,2}$. Consequently, the characteristic of mixtures with associated compounds is not the sign of $\Delta\eta_{1,2}$, but instead of its abnormally high absolute value. The above-mentioned difference between mixtures of benzene with aromatic and with aliphatic compounds is manifested in the case of viscosity by the fact that for mixtures of benzene with its halogenated derivatives $|\Delta\eta_{1,2}|$ increases in the order I > Br > Cl, and for mixtures of benzene with halogenated derivatives of butane, to the contrary, in the order Cl > Br > I.

Mixtures with associated components show a quantitative, and not a qualitative, difference from mixtures with normal compounds also in respect to the change in $\eta_{1,2}$ and $\Delta\eta_{1,2}$ with the temperature. In the studied temperature interval the $\eta_{1,2}$-t curves for all of the mixtures are convex to the temperature axis, the only difference being that the curves for the mixtures with associated compounds show a sharper deflection. For all of the studied mixtures the value $|\Delta\eta_{1,2}|$ decreases with increase in the temperature, in which connection this decrease is greater for both the mixtures with highly polar and associated compounds.

SUMMARY

1. The values of the dielectric permeability ($\epsilon_{1,2}$), density ($d_{1,2}$) and viscosity ($\eta_{1,2}$) for binary mixtures of benzene with various aliphatic and aromatic compounds were measured.

2. The mixtures composed of benzene and associated compounds (alcohols, acids, phenols, aniline) obey the same laws as do mixtures with normal compounds for the change in $d_{1,2}$, $\epsilon_{1,2}$ and $\eta_{1,2}$ with concentration and temperature, and show comparable deviations from additivity. The first mixtures differ from the second not in the laws of change, but only in the abnormal (when compounds of the same type are compared) values of the indicated constants and in their degree of change with concentration and temperature.

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EFFECT OF DILUTION ON THE ACTIVITY OF COPPER CATALYST IN THE DEHYDROGENATION OF BUTYL ALCOHOL

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In a previous communication [1] it was shown by one of us that in the dehydrogenation of butyl alcohol over copper catalyst it is possible to achieve a substantial increase in the yield of aldehyde if the starting alcohol is diluted with pure hydrogen in a mole ratio of 1 : 1. Such dilution during dehydrogenation is quite frequently used in industrial heterogeneous catalysis [2-7]. However, the dehydrogenation of alcohols in a stream of hydrogen has not been subjected to a systematic study, and only isolated statements can be found in the literature on the matter (for example, the dehydrogenation of octanol in a stream of hydrogen) [8].

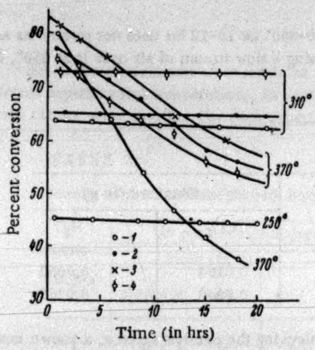

Fig. 1. Change of the percent conversion of butyl alcohol with time as a function of the experiment temperature and the addition of gaseous diluents. 1) Without gas addition, 2) with the addition of nitrogen, 3) with the addition of carbon dioxide; 4) with the addition of hydrogen.

It is assumed that the role played by added gases reduces to protecting the catalyst from poisoning [3, 7], either by suppressing side reactions that could lead to a poisoning of the catalyst surface [7], or by removing difficultly desorbed products, formed during reaction, from the surface [3, 9-11]. One of us had expressed the theory [11] that hydrogen plays the role of a catalyst in the acid-free esterification of alcohols, which takes place over dehydrogenation catalysts, and enters into the intermediate reactions.

In the present study we sought to determine whether the influence exerted by hydrogen in the dehydrogenation of alcohols is due to its specific action or whether it reduces to maintaining a constant catalyst activity; we also sought to determine whether other gases would exert a similar effect and to what a reduction in catalytic activity was due to. With this in mind we ran some experiments on the dehydrogenation of butyl alcohol over copper catalyst in the presence of various gases (hydrogen, nitrogen, carbon dioxide).

It must be remembered that the dehydrogenation of alcohols over copper catalyst is accompanied by acid-free esterification reactions, the result of further transformations of the aldehyde, and also by the formation of small amounts of butyric acid. For this reason we took as the criterion of catalyst activity in the dehydrogenation not the aldehyde yield, but instead the percent of alcohol conversion. Still, to more completely characterize the activity of the catalyst, we also took into consideration its activity in the acid-free esterification reaction, which made it possible to make some additional conclusions relative to the changes in the catalyst surface with time.

The experiments were run at 250, 310 and 370°, with a constant space velocity of 160. The method of operation was the same as that employed earlier [1]. The yields of the main reaction products as a function of the time and dilution with a gas (H_2, N_2, CO_2) are shown in Figs. 1 and 2.

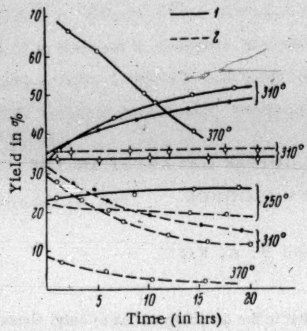

Fig. 2. Relationship between the yield of main reaction products and the time. 1) Aldehyde, 2) ester.

As can be seen from Figs. 1 and 2, at 250° the percent of alcohol conversion and the catalyzate composition fail to show any substantial change in 20 hrs of continuous catalyst operation even without the addition of any gas to the reaction zone.

At 310° in 30 hrs of catalyst operation without the addition of a gas the percent of alcohol conversion remains constant, but the ratio of the reaction products in the catalyzate changes substantially: the yield of aldehyde increases and the yield of ester decreases. The addition of nitrogen in a mole ratio of 1 : 1 is without effect on the operation of the catalyst. To the contrary, the addition of hydrogen in the same ratio assures a constant operation of the catalyst as regards the yields of aldehyde and ester.

At 370° the percent conversion drops quite sharply even after 9-10 hrs of catalyst operation. The addition of nitrogen, hydrogen or carbon dioxide retards the rate of catalyst deactivation. The nature of the gas is not important here. At the start of experiment (without the addition of a gas) there is a rapid increase in the aldehyde yield, corresponding to a slow increase at 310°, and then the aldehyde yield drops.

The blowing of the deactivated catalyst with hydrogen at 300-350° for 10-12 hrs does not restore its activity. However, the activity of the catalyst is completely restored by passing a slow stream of air over it at 250°, followed by reduction with hydrogen.

TABLE 1

Results of the Combustion of Two Weighed Samples of Catalyst

Time of catalyst operation (in hrs)	Weight of catalyst (in g)	Amount of substance consumed (in g)	Obtained (in g)	
			CO_2	H_2O
1	7.4	0.0066	0.0164	0.0052
15	6.9	0.0334	0.0840	0.0266

To establish the nature of the difficultly desorbed products blocking the catalyst surface, a known amount of the poisoned contact was combusted in a furnace set up for elemental analysis. In this way we were able to establish the presence of unsaturated compounds on the catalyst surface, to which the formula of $(C_4H_6O)_n$ could be assigned. The data on the combustion of two weighed samples of catalyst with a different degree of poisoning are given in Table 1.

Consequently, the following reactions proceed on the catalyst surface: 1) dehydration of alcohol to aldehyde, 2) acid-free esterification, in which the aldehyde participates, and 3) formation of high-molecular unsaturated compound.

The first two reactions represent stages in the acid-free esterification of alcohols, in which the aldehyde is an intermediate product. The reaction for the dehydrogenation of an alcohol to the aldehyde is monomolecular, and one active center is required for it to progress. A doublet is probably the active center here.

The ester condensation reaction is independent of whether it reduces to the condensation of two molecules of aldehyde or of a molecule of aldehyde and alcohol, it is bimolecular in nature, and it proceeds on two adjacent active centers, apparently, on two doublets. The difficultly desorbed compounds that are formed remain on the active centers of the surface and poison the catalyst. However, the process of poisoning the active centers proceeds by a law of chance, and here the number of adjacent pairs of active centers naturally decreases much more rapidly than does the total number of active centers. This is supported by the calculations of Rideal [12], who showed that to terminate the catalytic hydrogenation of benzene it is sufficient to poison only a part of the active centers. At the same time such a partially poisoned catalyst is still capable of catalyzing the hydrogenation of ethylene. This is associated with the fact that to hydrogenate benzene a sextet, which is composed of three adjacent doublets, is required, while to hydrogenate ethylene requires only one doublet.

In the presented experiments a reduction in catalyst activity is first manifested not in the total percent of alcohol conversion, but in a reduction in the yield of ester. Here an increase in the yield of aldehyde is observed, since the probability of its further transformation drops sharply due to the relatively rapid decrease in the number of adjacent pairs. Later, when a substantial portion of the active centers has become poisoned, both the total percent of conversion and the yield of aldehyde begin to decrease noticeably. At 310° in 30 hrs of catalyst operation we were unable to reach the point of a reduction in the aldehyde yield; however, this reduction was clearly expressed at a higher temperature (370°). Dilution with a gas reduces the partial pressure of all of the reactants and this is most strongly manifested in the case of the higher order reactions, and in particular, in the formation of the high-molecular compound.

That the influence of various gases proves to be extremely close at 370° is probably due to the fact that at high temperatures the adsorption of all of the indicated gases on copper is apparently slight, and all of the adsorption coefficients are close in their absolute values.

The situation is entirely different at lower temperatures (310°). Here the hydrogen plays a peculiar specific role. It apparently takes an active part in the acid-free esterification reaction as a supplemental catalyst, which is in agreement with the data of some earlier investigations made by one of us [11]. In addition, at lower temperatures hydrogen is capable of hydrogenating those unsaturated compounds whose condensation leads to the formation of high-molecular compounds, serving to poison the catalyst surface.

EXPERIMENTAL

All of the experiments were run in an aluminum block furnace, which made it possible to maintain a quite constant experimental temperature. As catalyst we took pure copper, which was prepared by the precipitation of cupric nitrate with caustic. For each experiment we took a fresh portion of catalyst, which was reduced with hydrogen at 200° until water ceased to evolve. Then the temperature was raised to the desired experimental temperature, and the addition of hydrogen was terminated if the experiment was run in the absence of hydrogen. The time of each experiment ranged from 10-30 hrs. Samples of the catalyzate were removed during experiment (at intervals of 1.5-2 hrs), and were analyzed separately.

TABLE 2

Results of the Experiments with Butyl Alcohol at 310°

Time (in hrs)	In presence of nitrogen				In presence of hydrogen			
	yield (in %)			percent conversion	yield (in %)			percent conversion
	aldehyde	ester	acid		aldehyde	ester	acid	
1	35.8	32.1	0.8	68.7	35.0	35.0	2.9	72.9
3	38.0	25.9	0.8	64.7	32.8	37.8	1.9	72.5
5	41.3	23.0	0.9	65.2	33.3	37.8	1.8	72.9
6	42.0	22.0	0.7	64.7	33.6	38.4	1.9	73.9
7	43.1	20.9	0.7	64.7	33.0	38.8	1.7	72.5
9	43.8	20.3	0.6	64.7	32.6	38.4	1.6	72.6
11	45.3	19.0	0.5	64.8	32.9	37.0	1.8	71.7
12	45.8	18.7	0.5	65.0	33.0	36.0	2.1	71.1
15	46.9	18.0	0.6	65.5	34.0	36.7	1.6	72.3

The liquid products were analyzed by conventional methods. In addition, the catalyzate was subjected to fractional distillation through a column with an efficiency of 18 theoretical plates. The reaction products were identified by their physical constants and by elemental analysis of the corresponding derivatives.

As an example we present the results of the experiments run at 310° in the presence of nitrogen and of hydrogen, with a constant space velocity of 160 (Table 2).

SUMMARY

1. The catalytic conversion of butyl alcohol over a copper catalyst was studied in the temperature range 250-370°, with dilution of the starting alcohol by various inert gases.

2. It was shown that the catalyst is deactivated during experiment due to the formation of difficultly desorbed products on its surface. The deactivation process can be retarded by the addition of gas diluents (nitrogen, hydrogen, carbon dioxide) to the starting alcohol. At high temperatures the nature of the gas diluent is not important. At lower temperatures (310°) a specific favorable influence is exerted by hydrogen on the retention of catalyst activity.

3. The functions of the catalyst change during the poisoning process, which is associated with the different orders of the reactions that progress on the catalyst surface.

4. An explanation of the observed rules was proposed.

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SOME N-ω-PHENYLALKYL-β-CHLOROPROPIONAMIDES

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In previous papers we have described the synthesis of a number of N-substituted β-chloropropionamides, containing benzyl and certain other radicals on the nitrogens [1, 2]. It was found that some of the obtained compounds are highly active anticonvulsants. It was also found that N-β-phenethyl-β-chloropropionamide (phenacon) is especially active in the treatment of tremors, in contrast to N-benzyl-β-chloropropionamide (chloracon), which is most active in the treatment of epileptic fits [3, 4].

In view of such a shift in the character of the anticonvulsant activity it seemed of interest to follow the effect of further lengthening of the alkyl chain separating the phenyl radical from the amido nitrogen on the physiological activity of N-substituted β-chloropropionamides.

With this in mind we synthesized the corresponding N-ω-phenylalkyl-β-chloropropionamides, and specifically: N-ω-phenylpropyl-β-chloropropionamide, N-ω-phenylbutyl-β-chloropropionamide and N-ω-phenylamyl-β-chloropropionamide. To determine the effect of other structural changes in the amide portion of the molecule we also synthesized N-phenylbutenyl-β-chloropropionamide and some other compounds.

All of the indicated compounds were synthesized by the scheme described by us earlier [1, 2], and specifically by the acylation of the corresponding amines with β-chloropropionyl chloride

$$RNH_2 + ClCOCH_2CH_2Cl \rightarrow RNHCOCH_2CH_2Cl$$

In the present paper we used a modified method and ran the acylation in a two-phase system by adding the acid chloride to a mixture composed of an ethyl acetate solution of the proper amine and an aqueous solution of sodium hydroxide. This permitted us to avoid a number of complications, and primarily a saponification of the acid chloride, which we observed when operating in an aqueous medium. With the indicated procedure the β-chloropropionamides were obtained in yields of 80-95%.

We used various methods to obtain the amines. ω-Phenylpropionamide (I) was obtained by hydrogenating the readily available β-phenylpropionitrile over skeletal nickel.

$$C_6H_6 + CH_2{=}CHCN \rightarrow C_6H_5CH_2CH_2CN \xrightarrow[Ni]{H_2} \underset{(I)}{C_6H_5CH_2CH_2CH_2NH_2}$$

To synthesize δ-phenylbutylamine (II) we used the following scheme:

$$C_6H_5CH{=}CHCHO + CH_3NO_2 \rightarrow \underset{(III)}{C_6H_5CH{=}CHCH{=}CHNO_2} \xrightarrow{LiAlH_4}$$

$$\rightarrow \underset{(IV)}{C_6H_5CH{=}CHCH_2CH_2NH_2} \xrightarrow[Pd/BaSO_4]{H_2} \underset{(II)}{C_6H_5CH_2CH_2CH_2CH_2NH_2}$$

The condensation of cinnamaldehyde with nitromethane in the presence of alcoholic caustic gave 1-phenyl-4-nitrobutadiene (III). The direct catalytic hydrogenation of the latter failed to yield (II), since here the process was accompanied by the formation of high-boiling products, which is probably linked with the condensations suffered by the nitrodiene under the hydrogenation conditions. Because of this we first reduced the nitrodiene (III) with aluminum lithium hydride, and the resulting δ-phenylbutenylamine (IV) was then converted to the unsaturated amine (II) by hydrogenation over palladium deposited on barium sulfate. The unsaturated amine (IV), obtained as an intermediate, was also used by us to obtain the corresponding N-substituted β-chloropropionamide for the purpose of determining the effect of a double bond in the alkyl chain on the physiological activity. The position of the double bond in the obtained δ-phenylbutenylamine cannot be considered as being rigidly established, but it is well known that when α,β-unsaturated nitro compounds are reduced with alumium lithium hydride it is the adjacent double bond that is reduced simultaneously with the nitro group [5, 6]. For this reason we believe that in the compound obtained by us it is the double bond in conjugation with the benzene ring that is retained, and therefore, the compound is 4-phenyl-3-butenylamine. The catalytic hydrogenation of the unsaturated β-chloropropionamide gave N-ω-phenylbutyl-β-chloropropionamide, completely identical with the product obtained by direct hydrogenation.

ω-Phenylamylamine (V) was synthesized by the following scheme:

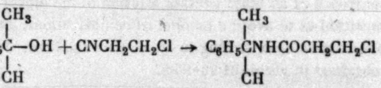
$$C_6H_5CH{=}CHCHO + CH_2(COOH)_2 \rightarrow \underset{(VI)}{C_6H_5CH{=}CHCH{=}CHCOOH} \xrightarrow[Ni]{H_2}$$

$$\rightarrow \underset{(VII)}{C_6H_5(CH_2)_4COOH} \rightarrow \underset{(VIII)}{C_6H_5(CH_2)_4CONH_2} \xrightarrow{LiAlH_4} \underset{(V)}{C_6H_5(CH_2)_5NH_2}$$

β-Styrylacrylic acid (VI), obtained by the condensation of cinnamaldehyde with malonic acid, was hydrogenated over nickel. The obtained ω-phenylvaleric acid (VII) was converted to the amide (VIII) via the corresponding acid chloride, which was not isolated. The reduction of the amide with lithium aluminum hydride led to obtaining (V) in a high yield.

In order to determine the effect of an additional phenyl radical in the amide portion of the molecule we synthesized N-β,β-diphenylethyl-β-chloropropionamide. The β,β-diphenylethylamine needed for this synthesis was obtained by the hydrogenation of diphenylacetonitrile, using the method recently described by one of us with M. I. Petruchenko [7].

Finally, to determine the effect of branching in the N-alkyl radical of the β-chloropropionamide, we synthesized N-α-phenylisopropyl-β-chloropropionamide. We used the Ritter reaction [8] to synthesize this compound, and the N-substituted β-chloropropionamide was obtained by reacting dimethylphenylcarbinol with β-chloropropionitrile.



$$C_6H_5\overset{\displaystyle CH_3}{\underset{\displaystyle CH}{C}}{-}OH + CNCH_2CH_2Cl \rightarrow C_6H_5\overset{\displaystyle CH_3}{\underset{\displaystyle CH}{C}}NHCOCH_2CH_2Cl$$

The use of β-chloropropionitrile in the Ritter reaction was previously unknown, and although the amide in which we were interested was obtained in very small yield here, still the method possesses definite advantages due to the simplicity and ready availability of the starting materials. The complications associated with the instability of β-chloropropionitrile under the conditions of the Ritter reaction are the reason for the low yield of the amide.

All of the synthesized N-substituted β-chloropropionamides were tested in the Pharmacological Section of our Institute by N. V. Kaverina. Of the synthesized compounds only the three saturated derivatives of N-ω-phenyl-β-chloropropionamide (Table, compounds 1, 2 and 4) show some activity in the treatment of convulsions produced by arecoline. Consequently, N-benzyl-β-chloropropionamide and N-β-phenylethyl-β-chloropropionamide, synthesized by us earlier, possess the optimum anticonvulsant activity.

EXPERIMENTAL

ω-Phenylpropylamine (I). Hydrocinnamonitrile was obtained by the literature method [9] in a yield of 60%; b. p. 100-102° (5 mm), $n^{19}D$ 1.5245.

A solution of 31.5 g of the nitrile in 100 ml of alcohol was hydrogenated in the presence of 15 g of skeletal nickel, and after the usual workup, we obtained 20.6 g (63.2%) of (I) with b. p. 78-80° (3 mm), $n^{20}D$ 1.5230.

Found %: N 9.88, 9.77. $C_9H_{13}N$. Calculated %: N 10.35.

The amine is a colorless liquid that avidly absorbs carbon dioxide from the air. From [10], b. p. 216-220°.

ω-Phenylbutylamine (II). 1-Phenyl-4-nitrobutadiene (III). A solution of 6.3 g of sodium hydroxide in 60 ml of methanol was added in drops, with vigorous stirring and cooling to 0°, to a solution of 20 g of freshly distilled cinnamaldehyde and 9.3 g of nitromethane in 75 ml of methanol. The reaction mixture was stirred for another 20 min at 0-5°, the precipitate of (III) sodium salt filtered, then washed with cold methanol, and finally it was suspended in a large volume of ice water and the suspension poured into 160 ml of 1 N hydrochloric acid, cooled to 0°. The crystalline precipitate of (III) was filtered, washed with cold water, dried in the air, and recrystallized from methanol. Yield 17.5 g (66%); yellow leaflets with m. p. 45-46°.

Found %: N 8.47, 8.26. $C_{10}H_9O_2N$. Calculated %: N 8.00.

4-Phenyl-3-butenylamine (IV). A solution of 12.8 g of (III) in 100 ml of ether was added with stirring and slight warming to an ether solution of lithium aluminum hydride (from 12.6 g of lithium hydride and 102 g of aluminum bromide in 260 ml of absolute ether), after which the mixture was heated under reflux for 4 hrs, stirred at room temperature for 5 hrs, and the excess aluminum hydride decomposed by the addition of 100 ml of moist ether, and then 20 mlof water. After this the reaction mixture was slowly poured with stirring into 10% hydrochloric acid (200 ml), cooled to 0°. The ether layer was separated and the water layer was first treated with excess concentrated caustic and then extracted with ether. The combined extracts were dried over sodium hydroxide, after which fractional distillation gave 10.5 g (77%) of (IV) with b. p. 90-91° (3.5 mm), $n^{27.5}$D 1.5548.

Found %: N 9.38, 9.67. $C_{10}H_{13}N$. Calculated %: N 9.52.

The compound is a colorless oil that instantly decolorizes permanganate solution.

The hydrochloride was obtained by saturating an ether solution of (IV) with dry hydrogen chloride. Colorless lustrous crystals with m. p. 219-221° (precipitation from methanol solution with ether).

Found %: Cl 19.48, 19.44. $C_{10}H_{14}NCl$. Calculated %: Cl 19.32.

The picrate was obtained in methanol solution; fine yellow crystals with m. p. 148-149° (from ether).

ω-Phenylbutylamine (II). A solution of 0.9 g of (IV) in 50 ml of anhydrous methanol was hydrogenated in the presence of 0.3 g of palladium-on-barium sulfate (5% palladium) at room temperature. The amount of hydrogen absorbed was 130 ml (0°, 760 mm); theory is 122 ml. After the usual workup we obtained 0.63 g (70%) of (II) with b. p. 87-88° (3.5 mm), n^{20}D 1.5200.

The compound is an oil with a slight odor which slowly absorbs carbon dioxide from the air.

Found %: N 9.12, 8.97. $C_{10}H_{15}N$. Calculated %: N 9.39.

From [11], b. p. 123-124° (17 mm).

The hydrochloride was obtained in conventional manner; colorless lustrous crystals with m. p. 162-163°.

Found %: Cl 18.90, 18.86. $C_{10}H_{16}NCl$. Calculated %: Cl 19.11.

Picrate: m. p. 120-124° (from anhydrous alcohol).

ω-Phenylamylamine (V). ω-Phenylvaleric acid (VII). 5 g of styrylacrylic acid, obtained by the Doebner method [12], was hydrogenated in 100 ml of anhydrous alcohol in the presence of 3 g of skeletal nickel at atmospheric pressure and room temperature. The hydrogenation was stopped after 1,470 ml of hydrogen had been absorbed, the catalyst removed by filtration, and after distilling off the alcohol we obtained 5.1 g (100%) of (VII) as colorless crystals with m. p. 57.5-58.5°. From [13], m. p. 58-59°.

ω-Phenylvaleramide (VIII). A mixture of 5 g of (VII) with 3.5 ml of thionyl chloride was heated on the water bath for 1 hr, then allowed to stand overnight, the excess thionyl chloride distilled off, and the residue poured into 20% aqueous ammonia solution; the obtained colorless crystals of (VIII) were filtered. Yield 4.0 g (80%); m. p. 104-106°. From [14]: m. p. 104-105°.

ω-Phenylamylamine (V). A suspension of 10.2 g of (VIII) in 200 ml of ether was added to a solution of 607 g of aluminum lithium hydride in 400 ml ether in 1 hr, the mixture stirred for another hour, and then the reaction was worked up as described above. Fractional distillation gave 4.5 (80%) of (V) with b. p. 88-89° (4 mm), $n^{20}D$ 1.5310.

Found %: N 8.32, 8.27. $C_{11}H_{17}N$. Calculated %: N 8.58. From [11], b. p. 131° (15 mm).

The amine is an oil with a slight odor which slowly absorbs carbon dioxide from the air.

The hydrochloride was obtained in conventional manner; colorless glistening leaflets with m. p. 150-151° (precipitation from methanol solution with ether).

Found %: Cl 17.75, 17.78. $C_{11}H_{18}NCl$. Calculation %: Cl 17.77.

N-Substituted-β-chloropropionamides. β-Chloropropionyl chloride (0.13 mole) was slowly added, with vigorous stirring and cooling to 0-5°, to a mixture of 0.13 mole of the amine in 100 ml of ethyl acetate and a solution of 5.3 g of sodium hydroxide in 50 ml of water. Then the pH of the mixture was adjusted to 7.5-8.0 by the addition of a small amount of caustic, and the stirring continued for another 30-40 min at room temperature. The ethyl acetate layer was separated, washed with water until neutral, then dried over sodium sulfate, the solvent vacuum-distilled, and the crystalline residue recrystallized from either alcohol or petroleum ether. The data on the compounds obtained by the described method are summarized in the table.

N-Substituted β-Chloropropionamides ($RNHCOCH_2CH_2Cl$)

Expt. no.	R	Yield (in %)	Melting point	Amount in %							
				C		H		N		Cl	
				found	calc.	found	calc.	found	calc.	found	calc.
1	$C_6H_5CH_2CH_2CH_2$	89	55—57° from alcohol	63.98, 64.01	63.88	7.33, 7.42	7.09	6.03, 6.13	6.20	15.52, 15.50	15.71
2	$C_6H_5CH_2CH_2CH_2CH_2$	87	45—46 from petroleum ether	—	—	—	—	6.16, 6.10	5.84	14.49, 14.76	14.79
3	$C_6H_5CH{=}CHCH_2CH_2$	77	95.5—100.5 from alcohol	—	—	—	—	5.79, 5.66	5.86	15.05, 14.79	14.92
4	$C_6H_5CH_2CH_2CH_2CH_2CH_2$	95	56—57 from petroleum ether	66.30, 66.34	66.30	8.00, 7.86	7.88	5.80, 5.77	5.52	14.08, 14.11	13.97
5	$(C_6H_5)_2CHCH_2$	90	112—113.5 from alcohol	—	—	—	—	4.85, 4.62	4.86	12.41, 12.54	12.36

Hydrogenation of N-ω-phenylbutenyl-β-chloropropionamide. A solution of 0.5 g of the compound in 10 ml of alcohol was hydrogenated in the presence of 0.2 g of palladium-on-barium sulfate at atmospheric pressure and room temperature. The hydrogenation was stopped after the theoretical amount of hydrogen had been absorbed, and the usual workup gave 0.45 g (90%) of N-ω-phenylbutyl-β-chloropropionamide. Recrystallization from alcohol gave the compound as colorless crystals with m. p. 44-45°. The melting point was not depressed when the compound was mixed with the compound obtained by the acylation of δ-phenylbutylamine.

N-δ-Phenylisopropyl-β-chloropropionamide. To a solution of 16.2 g of dimethylphenylcarbinol and 10.5 g of β-chloropropionitrile in 30 ml of glacial acetic acid, with stirring and cooling, was slowly added 6 ml of concentrated sulfuric acid, and then the mixture was allowed to stand overnight. The two-layer reaction mixture was poured into 500 ml of water, the acid neutralized with soda, the product extracted with ether, the ether extracts dried over magnesium sulfate, and the ether removed by distillation. The residue was distilled at 0.1 mm, collecting the fraction with b. p. 80-110°, and contained a crystalline product as impurity; the latter was removed by adding petroleum ether to the distillate; yield 1.2 g (5%). Colorless glistening crystals with m. p. 90-91° (from alcohol).

Found %: N 6.10, 6.17; Cl 15.78, 15.85. $C_{12}H_{16}ONCl$. Calculated %: N 6.26; Cl 15.71.

SUMMARY

Some N-ω-phenylalkyl-β-chloropropionamides and related compounds were synthesized, and their pharmacological activity was investigated. The acylation of the arylalkylamines with β-chloropropionyl chloride was run in a two-phase system (ethyl acetate-water) in the presence of sodium hydroxide.

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REACTION OF p-HALOPHENYLHYDRAZINES WITH ARSENIC ACID

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Earlier it had been shown that the reaction of arsenic acid with phenylhydrazine (in aqueous solution), depending on the experimental conditions, gives in good yields phenylarsine oxide, diphenylarsine oxide and triphenylarsine oxide, provided the reaction is run in the presence of copper or its salts [1].

It seemed of interest to us to determine to what extent this reaction is general for the preparation of other substituted arylarsine oxides. To answer this we decided to investigate the possibility of forming arylarsine oxides with halogen atoms in the para-position to the arsenic radical. For this purpose we reacted p-chloro-, p-bromo- and p-fluorophenylhydrazine with arsenic acid.

The proper hydrazine was gradually added with stirring to a heated water solution of arsenic acid, to which copper bronze had been previously added.

It proved that both p-chloro- and p-bromophenylhydrazine react in normal manner, similar to phenyl- and tolylhydrazine, and give the corresponding substituted arylarsine oxides as the final product. After the workup, described in detail in the Experimental section, we isolated (p-chlorophenyl) dichloroarsine and chlorodi-(p-chlorophenyl) arsine. In the reaction with the bromophenylhydrazine we isolated chlorodi-(p-bromophenyl) arsine, which in turn was converted to the corresponding acid by oxidation with hydrogen peroxide.

With this method we were also able to obtain chlorodi-(p-fluorophenyl) arsine from p-fluorophenylhydrazine, which on subsequent oxidation was converted to the corresponding di-(p-fluorophenyl) arsenic acid.

Mention should be made of some of the properties of the fluoro-substituted aromatic arsenic compounds. Thus, chlorodi-(p-fluorophenyl) arsine is much more difficult to oxidize than the corresponding chlorophenyl and bromophenyl derivatives.

Hydrogen peroxide is a poor oxidizing agent here, and we were able to obtain much better results by using nitric acid (d 1.4) as the oxidizing agent.

It is interesting to mention that the constants of the p-fluoro derivatives of arylarsenic compounds prove to be very close to the corresponding constants of the phenyl derivatives of arsenic.

EXPERIMENTAL

Oxidation of p-chlorophenylhydrazine with arsenic acid. To a solution of 70 g of arsenic acid in 210 ml of water, heated to 70°, to which 3 g of copper bronze had been previously added, was gradually added with good stirring 40 g of p-chlorophenylhydrazine. The reaction was ended in 2 hrs, and here a heavy oil collected on the bottom of the flask. The water layer was decanted from the oil, and the oil was shaken with fuming hydrochloric acid to convert the arsenic oxides to the chlorides. The (p-chlorophenyl) dichloroarsine and chlorodi-(p-chlorophenyl) arsine obtained here were then fractionally distilled.

Two fractions were collected: 1st, 160-170° (20 mm), 6 g, and 2nd, 180-240° (20 mm) (main portion distilled at 225°), 17 g. At atmospheric pressure the 1st fraction distilled mainly at 277°, which corresponds to the boiling point of (p-chlorophenyl) dichloroarsine. For further identification the chloride was hydrolyzed with aqueous ammonia solution. The thus obtained oxide after recrystallization from benzene had m. p. 184°, which corresponds to the melting point of p-chlorophenylarsine oxide. The 2nd fraction was redistilled and boiled at

225° (15 mm). The distillate on cooling solidified to a crystalline mass with m. p. 51° (from the literature [4], m. p. 51°).

Oxidation of p-bromophenylhydrazine with arsenic acid. The experiment was run using the conditions described above. The following fractions were collected: 1st, 117-130° (0.4-0.8 mm), 7.8 g, and 2nd, 138-165° (0.4-0.8 mm), 9.0 g.

To effect a better separation of the primary and secondary arsenic compounds, both fractions were oxidized with hydrogen peroxide and converted to the corresponding acids. After recrystallization of the products of the oxidation of the 1st fraction from alcohol we obtained colorless crystals of p-bromophenylarsenic acid, which proved to be difficultly soluble in water, alcohol and other organic solvents, and did not melt when heated to 280°. The oxidation product of the 2nd fraction proved to be di-(p-bromophenyl) arsenic acid. It crystallizes from boiling alcohol as colorless prisms (m. p. 186-187°), and is very difficultly soluble in water, acetone, chloroform and petroleum ether.

Found %: As 17.80. $C_{12}H_9O_2Br_2As$. Calculated %: As 17.86.

To obtain the pure chloride we took the di-(p-bromophenyl)-arsenic acid and converted it to the chloride by reduction with sulfur dioxide in concentrated hydrochloric acid in the presence of potassium iodide. The obtained oil solidified and was recrystallized from alcohol. The chloride was obtained as well-shaped crystals with m. p. 57-58°.

Found %: As 17.50. $C_{12}H_8ClBr_2As$. Calculated %: As 17.75.

Oxidation of p-fluorophenylhydrazine with arsenic acid. The starting product for the preparation of p-fluorophenylhydrazine was p-fluoronitrobenzene, which we obtained by reacting a concentrated solution of p-nitrobenzenediazonium sulfate with concentrated hydrofluoric acid at the boil [2]. However, the conditions for the diazotization of p-nitroaniline, recommended by Holleman and Beekman to obtain a concentrated solution of the diazonium sulfate, give much difficulty in that each drop of the nitrite causes a slight explosion. Consequently, we were forced to run the diazotization in less concentrated media, which proved to be more practical. The fluoronitrobenzene was converted to the fluorophenylhydrazine through p-fluoroaniline [3]. Then 31 g of p-fluorophenylhydrazine was oxidized with a hot solution of 71 g of arsenic acid in 213 ml of water under the conditions described in the preceding experiment. The obtained organoarsenic oxides were then converted to the chlorides, and after the usual workup, the lattter were fractionally distilled at 12 mm, where the following fractions were collected: 1st, 132-150° (mostly at 140-145°), 4 g; 2nd, 160-170° (mostly at 162-164°), 12 g; and 3rd, 170-176°, 5.2 g.

To obtain complete separation, the different chloride fractions were converted to the acids. Very little reaction occurred when we attempted to oxidize the 2nd fraction with hydrogen peroxide; vigorous reaction occurred when we used nitric acid (d 1.4) and a solid product was formed. Recrystallization of the solid from a large volume of boiling water gave long colorless prismatic crystals with m. p. 136-138°. The compound is very difficultly soluble in cold water, and readily soluble in hot alcohol.

Based on the analysis data, the compound proved to be di-(p-fluorophenyl) arsonic acid.

Found %: As 24.80. $C_{12}H_9O_2F_2As$. Calculated %: As 25.17.

To obtain chlorodi-(p-fluorophenyl) arsine the recrystallized acid was converted to the chloride by reduction with sulfur dioxide in strong hydrochloric acid. The obtained oil distilled at 156-157° at 13 mm. On cooling the oil solidified and after recrystallization from alcohol was obtained as colorless crystals with m. p. 39°.

Found %: Cl 11.86. $C_{12}H_8F_2ClAs$. Calculated %: Cl 11.76.

SUMMARY

On the examples of p-Br-, p-Cl- and p-F-phenylhydrazines it was shown that the preparation of organoarsenic compounds from arylhydrazines and arsenic acid in the presence of metallic copper is a general reaction.

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NEW METHOD FOR THE PREPARATION OF ORGANOARSENIC COMPOUNDS BY THE OXIDATION OF A MIXTURE OF PHENYLHYDRAZINE AND ARSENIC TRICHLORIDE WITH ATMOSPHERIC OXYGEN IN THE PRESENCE OF CUPRIC CHLORIDE

A. B. Bruker and N. M. Nikiforova

Wieland and Madelung [1], in oxidizing phenylhydrazine with phenylarsenic and diphenylarsenic acid, obtained triphenylarsine. Attempts to isolate organoarsenic compounds when phenylhydrazine was oxidized with arsenic acid proved unsuccessful.

Zeide, Sherlin and Bras [2], on reacting phenyl- or tolylhydrazine in aqueous solution with arsenic acid in the presence of copper or its salts, obtained a mixture of phenyl- or tolylarsine oxide, diphenyl- or ditolylarsine oxide and triphenyl- or tritolylarsine. This same method was also used to obtain the p-chloro-, p-bromo- and p-fluorophenylarsenic compounds [3].

In a paper by Bruker and Makliaev [4] on the role of copper in obtaining aromatometallic compounds by either the diazo or hydrazino reaction it was shown that if an inorganic arsenic compound is the starting product, then to obtain aromatoarsenic componds it is necessary to have copper present. If it is aromatic arsenic compounds that are subjected to arylation, then this reaction also goes in the absence of a special catalyst. Consequently, the difference between the reaction of Zeide, Sherlin and Bras and that of Wieland and Madelung consists only in the use of copper or its salts as catalyst.

In previous papers we have described a new method for the preparation of aromatic compounds of antimony, consisting in the reaction of an arylhydrazine with antimony trichloride [5] or with antimony pentachloride [6] in hydrochloric acid medium in the presence of cupric chloride, in which connection atmospheric oxygen is the oxidizing agent in this reaction.

In the present paper our goal was to investigate the possibility of obtaining aromatoarsenic compounds by the same method that we used earlier to synthesize aromatoantimony compounds. Actually, when phenylhydrazine hydrochloride (1 mole) was reacted with arsenic trichloride (1 mole) in hydrochloric acid medium in the presence of cupric chloride and atmospheric oxygen we obtained phenyldichloroarsine in 58-65% yield (based on arsenic trichloride).

The formation of phenyldichloroarsine in this reaction can be depicted as follows: phenylhydrazine hydrochloride is oxidized by atmospheric oxygen in the presence of cupric chloride to benzenediazonium chloride, and the latter then reacts with arsenic trichloride to give the intermediate binary compound.

$$C_6H_5NHNH_2 \cdot HCl + AsCl_3 + O_2 \xrightarrow{CuCl_2} C_6H_5N_2Cl \cdot AsCl_3 + 2H_2O$$

A second molecule of phenylhydrazine reduces the binary compound to phenyldichloroarsine, and is itself oxidized to benzenediazonium chloride.

$$2C_6H_5N_2Cl \cdot AsCl_3 + C_6H_5NHNH_2 \cdot HCl \xrightarrow{CuCl_2} 2C_6H_5AsCl_2 + C_6H_5N_2Cl + 2N_2 + 4HCl$$

The following facts serve as proof of this. Phenyldichloroarsine is formed when phenylhydrazine hydrochloride is reacted under the above-described conditions with the binary compound $C_6H_5N_2Cl \cdot AsCl_3$, obtained directly from benzenediazonium chloride and arsenic trichloride. As regards the indicated intermediate binary compound, then we found it impossible to isolate it from the reaction mixture obtained in the reaction with phenylhydrazine. However, as evidence that it is formed is the fact that the binary compound $C_{10}H_7N_2Cl \cdot AsCl_3$ is obtained when β-naphthylhydrazine is reacted with $AsCl_3$ under similar conditions.

Together with phenyldichloroarsine, diphenylchloroarsine is formed in the reaction of arsenic trichloride with phenylhydrazine and benzenediazonium chloride.

The formation of diphenylchloroarsine in this reaction is apparently due to the fact that phenyldichloroarsine, partially dissolving in the aqueous hydrochloric acid reaction solution, gives the binary compound $C_6H_5N_2Cl \cdot C_6H_5AsCl_2$ with benzenediazonium chloride, which is then reduced by phenylhydrazine to diphenylchloroarsine.

$$C_6H_5N_2Cl + C_6H_5AsCl_2 \rightarrow C_6H_5N_2Cl \cdot C_6H_5AsCl_2,$$

$$2C_6H_5N_2Cl \cdot C_6H_5AsCl_2 + C_6H_5NHNH_2 \cdot HCl \xrightarrow{CuCl_2}$$

$$\rightarrow 2(C_6H_5)_2AsCl + C_6H_5N_2Cl + 2N_2 + 4HCl$$

It could be postulated that if the reaction was run in alcoholic hydrochloric acid medium, in which phenyldichloroarsine is much more soluble than in aqueous hydrochloric acid solution, then the yield of diphenylchloroarsine should increase due to the fact that here more favorable conditions exist for the formation of the binary compound $C_6H_5N_2Cl \cdot C_6H_5AsCl_2$.

Actually, a mixture of phenyldichloroarsine and diphenylchloroarsine, with a predominance of the diphenylchloroarsine, is formed when phenylhydrazine hydrochloride (2.2 moles) is reacted with arsenic trichloride (1 mole), or when a mixture of phenylhydrazine hydrochloride and benzenediazonium chloride is reacted with arsenic trichloride, in alcoholic hydrochloric acid medium in the presence of cupric chloride and atmospheric oxygen.

The results of our experiments, in which the reaction of benzenediazonium chloride with phenyldichloroarsine in alcoholic hydrochloric acid medium gave the binary compound of benzenediazonium chloride and phenyldichloroarsine $C_6H_5N_2Cl \cdot C_6H_5AsCl_2$, from which secondary aromatoarsenic compounds are subsequently formed, can serve as evidence that the formation of secondary aromatoarsenic compounds goes through the binary compound of type $ArN_2Cl \cdot ArAsCl_2$.

Since diphenylchloroarsine is practically insoluble in alcohol hydrochloric acid medium, it fails to react with benzenediazonium chloride to give the binary compound $(C_6H_5)_2AsCl \cdot C_6H_5N_2Cl$, from which it is possible to obtain tertiary arsines. This is probably the reason why we were unable to find any tertiary arsines in the reaction mass when using our method.

Consequently, the mechanism proposed by us earlier for the formation of aromatic compounds of arsenic and antimony via the diazo reaction [7] is again confirmed in the present study.

EXPERIMENTAL

I. Reaction of arsenic trichloride with phenylhydrazine in hydrochloric acid medium in the presence of catalysts and atmospheric oxygen. Into a 500-ml flask, fitted with seal-stirrer, two spargers and a reflux condenser, was charged arsenic trichloride (18 g), hydrochloric acid (80 ml, d 1.19), phenylhydrazine (11 g), water (225 ml) and catalysts (0.5 g of cupric chloride and 3 g of ferric chloride). The stirrer was turned on, and the top of the reflux condenser was connected to a water-jet pump to suck air through the reaction mixture. The heavy oil that separated after stirring for 36 hrs was separated from the liquid. The crude phenyldichloroarsine weighed 15 g (65.5%, based on arsenic trichloride). Vacuum-distillation gave 13 g (58%, based on arsenic trichloride) of phenyldichloroarsine with b. p. 116° (6 mm).

II. Preparation of binary compound of β-naphthalenediazonium chloride with arsenic trichloride from β-naphthylhydrazine hydrochloride and arsenic trichloride in hydrochloric acid medium. To a solution of 6.6 g of arsenic trichloride in 100 ml of hydrochloric acid (d 1.19) was added 0.5 g of cupric chloride and 0.5 g of ferric chloride. When the arsenic trichloride, cupric chloride and ferric chloride had dissolved, 4 g of β-naphthylhydrazine hydrochloride was added in small portions and with good stirring. After stirring for an hour a test with β-naphthol gave the diazo reaction. The stirring was continued for 45 hrs. The obtained yellow-green precipitate was suction-filtered, and then washed with hydrochloric acid (d 1.19) and absolute ether. Yield 7.2 g (64%, based on arsenic trichloride).

Found %: As 19.81, 19.35; N 6.92, 7.21; Cl 38.05, 38.93. $C_{10}H_7Cl_4N_2As$. Calculated %: As 20.17; N 7.53; Cl 38.70.

Decomposition of the binary compound with dilute ammonia solution gave β-naphthylarsenic acid (yield about 50%), which when reduced with SO_2 in hydrochloric acid medium gave β-naphthyldichloroarsine with m. p. 67-68°.

III. Preparation of a mixture of phenyldichloroarsine and diphenylchloroarsine. a) Preparation of binary compound $C_6H_5N_2Cl \cdot AsCl_3$.* Arsenic trichloride (36.6 g) was added with stirring to a solution of 25.9 g of aniline hydrochloride in 130 ml of anhydrous alcohol. The obtained mixture was diazotized under cooling (1-3°) with isoamyl nitrite (23.3 g). The reaction was run in a closed vessel, fitted with a mercury-seal stirrer, dropping funnel and reflux condenser. After diazotization the reaction mass was stirred for 10 min. Then the filtrate was removed by rapid suction-filtration, while the precipitate was washed several times with absolute ether and then dried in a desiccator over sulfuric acid. The yield of product was 44.1 g (65% based on arsenic trichloride).

Found %: As 23.02, 22.55; N 8.63, 8.55. $C_6H_5Cl_4N_2As$. Calculated %: As 23.29; N 8.70.

The compound was obtained as a white crystalline powder, which soon turned yellow. It gives the diazo reaction with β-naphthol. On standing it suffers partial decomposition, accompanied by the formation of chlorobenzene. M. p. 83-85° (with decomp.). The compound is soluble in water, hydrochloric acid and alcohol, and insoluble in absolute ether. It decomposes with the evolution of nitrogen in the presence of copper in alcohol, acetone or glacial acetic acid, and also when heated with dilute hydrochloric acid or water.

b) Decomposition of the complex $C_6H_5N_2Cl \cdot AsCl_3$ in order to obtain aromatoarsenic compounds. A mixture of binary compound $C_6H_5N_2Cl \cdot AsCl_3$ (22 g) and cupric chloride (0.2 g) was dissolved in dilute hydrochloric acid (1 : 3) in an open flask with stirring. Then phenylhydrazine hydrochloride (9 g) was added to the solution and the reaction mass was stirred for 20 hrs. The oily product (14 g) was separated from the liquid. The oil was dissolved in hot alcohol (60 ml). The alcohol solution was then added to 125 ml of 5% ammonia, and the obtained mass of oxides, after separation from the liquid, was treated with hot concentrated hydrochloric acid (50 ml, d 1.19). The weight of the product after treatment was 8.7 g. Fractional distillation gave two fractions: 1st, phenyldichloroarsine, 127-129° (13 mm), 4.3 g; and 2nd, diphenylchloroarsine, 172-175° (11 mm), 4.2 g. The 2nd fraction crystallized when cooled and seeded. After recrystallization from alcohol the product had m. p. 38-39°. The yield of distilled diphenylchloroarsine was 25.6% (based on arsenic trichloride). The yield of distilled phenyldichloroarsine was 31.1% (based on arsenic trichloride).

IV. Reaction of arsenic trichloride, benzenediazonium chloride and phenylhydrazine hydrochloride in hydrochloric acid medium in the presence of catalysts. a) Preparation of the binary compound $C_6H_5N_2Cl \cdot AsCl_3$ and its solution. A solution of benzenediazonium chloride was added in drops to a mixture of arsenic trichloride (18.1 g) and hydrochloric acid (50 ml, d 1.19). The obtained precipitate of binary compound $C_6H_5N_2Cl \cdot AsCl_3$ was dissolved by the addition of dilute hydrochloric acid (200 ml).

b) Preparation of phenyldichloroarsine and diphenylchloroarsine. The solution obtained in a) was treated with 12 g of phenylhydrazine hydrochloride and 1 g of ferric chloride. Then a solution of 0.5 g of cupric chloride in 10 ml of hydrochloric acid (1 : 2) was added in 20 min. The reaction was run with cooling and stirring. After stirring for 12 hrs the oily product was separated from the liquid. The oil weighed 25 g. The oil was treated with 50 ml of benzene, and the benzene solution was dried over calcium chloride. After removal of the benzene by distillation the residue was vacuum-distilled: 1st fraction, phenyldichloroarsine, 130-135° (10-12 mm), 15.4 g; 2nd fraction, diphenylchloroarsine, 165-170° (10-12 mm), 3 g. The yield of distilled phenyldichloroarsine, based on arsenic trichloride, was 69.5%. The yield of diphenylchloroarsine was 11.3%.

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* Done jointly with N. M. Korneichuk.

V. Reaction of arsenic trichloride with phenylhydrazine hydrochloride in alcohol-hydrochloric acid medium in the presence of cupric chloride. The experiment was run using the same apparatus as in Expt. I. Into the reaction flask was charged water (150 ml), hydrochloric acid (50 ml, d 1.19), arsenic trichloride (18 g), phenylhydrazine hydrochloride (33 g), alcohol (200 ml) and cupric chloride (1 g). The reaction was run at 50° with the passage of air through the mixture. After stirring for 39 hrs the oily product was separated from the alcohol-hydrochloric acid solution. The crude product weighed 15 g. Vacuum-distillation gave two fractions: 1st (phenyldichloroarsine), 130° (10 mm), 3.3 g; 2nd (diphenylchloroarsine), 202-220° (16 mm), 7.3 g. The 2nd fraction crystallized on cooling, and the crystals melted at 36°. The yield of distilled phenyldichloroarsine, based on arsenic trichloride, was 14.8%. The yield of distilled diphenylchloroarsine, also based on arsenic trichloride, was 28%.

VI. Reaction of arsenic trichloride, benzenediazonium chloride and phenylhydrazine hydrochloride in the presence of catalysts. A mixture of arsenic trichloride (18.1 g) and hydrochloric acid (50 ml, d 1.19) was charged into a stoppered flask, fitted with a seal-stirrer and a wide tube for adding the reactants. The mixture was cooled to 2-3° and then a solution of benzenediazonium chloride, obtained by the diazotization of 9.3 g of aniline with a solution of 7.5 g of sodium nitrite in 13 ml of water and dilute hydrochloric acid (26 ml of hydrochloric acid and 30 ml of water), was added in drops with stirring. The formation of a precipitate was observed here, the color of which ranged from yellowish to pink.

Phenylhydrazine (12 g), methyl alcohol (250 ml) and ferric chloride (1 g) were then added to the reaction mixture. The reaction was run with cooling and stirring. A solution of cupric chloride (0.5 g in 10 ml of hydrochloric acid; 1 : 2) was added to the reaction mass in 15-20 min. After stirring for 6 hrs the oily product was separated from the liquid and washed several times with 2% hydrochloric acid. The crude product weighed 16.3 g. The product was treated with 50 ml of benzene, and the benzene solution was dried over calcium chloride. The benzene was distilled off and the residue was vacuum-distilled: 1st fraction, phenyldichloroarsine, 130-135° (10-15 mm), 1.8 g (8%, based on taken $AsCl_3$); 2nd fraction, diphenylchloroarsine, 178-182° (10-12 mm), 10.6 g (40%, based on taken $AsCl_3$).

VII. Reaction of benzenediazonium chloride and phenyldichloroarsine in alcoholic medium. * a) Preparation of binary compound $C_6H_5N_2Cl \cdot C_6H_5AsCl_2$. Phenyldichloroarsine (16.5 g) was added with stirring to an alcohol solution of 6.5 g of aniline hydrochloride. The solution was cooled to 3° and then diazotized with 6.8 g of amyl nitrite. The obtained pink crystalline precipitate was suction-filtered rapidly, washed 3 times with absolute ether, and dried in a vacuum-desiccator. The obtained binary compound weighed 6.5 g. The odorless, cream-colored crystals partially decomposed on standing with the liberation of chlorobenzene. The binary compound $C_6H_5N_2Cl \cdot C_6H_5AsCl_2$ is soluble in ethyl and methyl alcohols, and difficultly soluble in carbon tetrachloride, acetone and chloroform. M. p. 88-90° (with decomp.).

Found %: Cl 28.64, 29.02; As 19.23, 18.70; N 7.54, 8.31, 8.06. $C_{12}H_{10}Cl_3N_2As$. Calculated %: Cl 29.30; As 20.64; N 7.69.

b) Preparation of diphenylarsenic acid from binary compound $C_6H_5N_2Cl \cdot C_6H_5AsCl_2$. The binary compound $C_6H_5N_2Cl \cdot C_6H_5AsCl_2$ (1.6 g) was added gradually to a solution of 3 g of sodium bicarbonate in 100 ml of water. The reaction was accompanied by the evolution of nitrogen. On conclusion of reaction the solution was evaporated to a volume of 75 ml, filtered, and the filtrate acidified with hydrochloric acid. The obtained precipitate of diphenylarsenic acid weighed 0.65 g, and after recrystallization from water had m. p. 173°. Yield 56.5% (based on arsenic).

VIII. Preparation of diphenylchloroarsine from phenyldichloroarsine and benzenediazonium chloride without isolation of the binary compound $C_6H_5N_2Cl \cdot C_6H_5AsCl_2$. A solution of 8 g of aniline hydrochloride in 15 ml of hydrochloric acid (d 1.19) and 20 ml of ethyl alcohol was diazotized under cooling and stirring with a solution of 5 g of sodium nitrite in 10 ml of water. Then 12.4 g of phenyldichloroarsine, 0.3 g of copper sulfate and 2% sodium hydroxide solution was gradually added to the benzenediazonium chloride until the reaction was neutral. The evolution of nitrogen was observed here. Caustic was then added until the reaction was alkaline and after stirring for 12 hrs the mixture was filtered and the filtrate acidified with 5 N hydrochloric acid. The obtained precipitate of phenylarsenic acid was suction-filtered. Yield 8.5 g (61%). The acid was reduced with sulfur dioxide in hydrochloric acid medium (in the presence of KI). We obtained 7.12 g (48.5%) of diphenylchloroarsine with m. p. 36°.

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* Done jointly with O. O. Kovtun.

IX. Reaction of binary compound $C_6H_5N_2Cl \cdot AsCl_3$ with phenylhydrazine hydrochloride in alcohol-hydrochloric acid medium in the presence of cupric chloride and ferric chloride. The reaction was run in the apparatus described in Expt. I. A solution of binary compound $C_6H_5N_2Cl \cdot AsCl_3$ (16 g), cupric chloride (0.5 g) and ferric chloride (1.5 g) in dilute hydrochloric acid (150 ml, 1 : 3) was prepared. Phenylhydrazine hydrochloride (7.2 g) was then gradually added to the obtained solution with stirring. The reaction mixture was stirred. Alcohol (150 ml) was gradually added through a dropping funnel. After vigorous stirring for 4 hrs the reaction mixture was allowed to stand overnight. The obtained oil was separated from the liquid. The crude product weighed 8.6 g. The product crystallized in a cooling mixture, but melted at room temperature. The crude product was dissolved in hot alcohol (60 ml) and then hydrolyzed with 5% ammonia (80 ml) with shaking. The obtained red mass of oxides was treated with 30% caustic (15 ml) with heating to 90°. The insoluble diphenylarsine oxide was separated, and then washed in the cold with 30% caustic and water. The yield of diphenylarsine oxide was 5 g (42.5%, based on $AsCl_3$).

From 5 g of $[(C_6H_5)_2As]_2O$ we obtained 3.6 g (27.5%, based on $AsCl_3$) of diphenylchloroarsine with m. p. 37°. Dilution of the alkaline filtrate with water, followed by acidification until weakly acid, gave 1.3 g (15.5%, based on inorganic arsenic) of phenylarsine oxide. From 1.3 g of C_6H_5AsO we obtained 0.9 g (8.1%, based on consumed $AsCl_3$) of phenyldichloroarsine.

SUMMARY

It was shown that the reaction of phenylhydrazine and arsenic trichloride in hydrochloric acid medium in the presence of cupric chloride and atmospheric oxygen yields primary and secondary aromatoarsenic compounds. A mechanism for the reaction was postulated and verified experimentally.

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PREPARATION OF ESTERS OF FLUOROANTIMONIOUS AND FLUOROTITANIC ACIDS BY TREATMENT OF THE COMPLETE ESTERS OF THESE ACIDS WITH ANTIMONY TRIFLUORIDE

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In the series of esters of titanic and antimonious acids, complete esters of these acids and certain chloro-, bromo-, and iodo-derivatives of titanium and antimony have been described. Alkoxy titanium fluorides and alkoxyfluorostibines have not been described up to now.

In the present work the reactions of antimony trifluoride with the complete esters of titanic and antimonious acids were studied; as we showed, they led to the formation of alkoxytitanium fluorides and alkoxyfluorostibines.

Similar reactions (the opposite of the disproportionation) have been widely used for the preparation of alkoxychloro-derivatives. In particular, the preparation of various alkoxytitanium chlorides through the reaction of titanium tetrachloride with alkyl orthotitanates has been described by A. N. Nesmeianov, R. Kh. Freidlina, and co-workers [1].

We found that in the reaction of antimony trifluoride with alkoxystibines, dialkoxyfluorostibines of the type $(RO)_2SbF$ (where $R = C_2H_5$, iso-C_3H_7) could be obtained in satisfactory yields. In this case it was established that double compounds having the hypothetical structure $Sb(OR)_3 \cdot 3Sb(OR)_2F$ can be isolated as intermediate products of this reaction; on subsequent heating in vacuo these compounds dissociate and give a dialkoxyfluorostibine and a trialkoxystibine, which are separated by distillation.

Thus on heating a mixture of triethoxystibine (3 moles) and antimony trifluoride (1 mole) to 150°, there was isolated a solid, homogeneous product melting at 56-59° and, according to analytical data, corresponding to the composition

$$SbF_3 \cdot 3Sb(OC_2H_5)_3 \qquad (1)$$

However, a closer study of this product made it possible to propose a structure for it, corresponding to the double compound

$$Sb(OC_2H_5)_3 \cdot 3Sb(OC_2H_5)_2F \qquad (2)$$

In particular, the fact that an identical compound is obtained in the reaction of 3 moles of diethoxyfluorostibine with 1 mole of triethoxystibine may serve as a certain confirmation. Besides this, it is possible that the formation of the indicated double compound (2) is the result of a secondary process and that complex (1) is first formed.

On distillation in vacuo of the double compound (2) or the reaction mixture obtained in the reaction of triethoxystibine and antimony trifluoride, diethoxyfluorostibine and triethoxystibine were isolated.

Diisopropoxyfluorostibine was prepared similarly. In this case the latter was separated with difficulty from triisopropoxystibine, which has nearly the same boiling point, on distillation of the reaction mixture in vacuo. The alkoxyfluoro-derivative was isolated from the distillate by freezing.

This method of preparing alkoxyfluoro-derivatives proved applicable also in those cases in which antimony trifluoride is made to react with alkoxy-derivatives of titanium. Thus, when antimony trifluoride was heated with various alkyl orthotitanates, the corresponding trialkoxytitanium fluorides were obtained. In this case double compounds of the type $Sb(OR)_3 \cdot 3Ti(OR)_3F$ (3) also were isolated as intermediate products of this reaction.

The reaction may be represented by the following scheme, from which it is evident that this process may be used both for the synthesis of alkoxytitanium fluorides and for the preparation of trialkoxystibines.

$$3Ti(OR)_4 + SbF_3 \rightarrow Sb(OR)_3 \cdot 3Ti(OR)_3F \rightarrow 3Ti(OR)_3F + Sb(OR)_3$$

Triethoxy-, triisopropoxy-, and tributoxytitanium fluorides were prepared in this way. The first two are crystalline substances; the last is a colorless liquid.

The intermediate double compounds (3) obtained from ethyl and isopropyl orthotitanates are solid substances, whereas that from butyl orthotitanate is a liquid.

In order to confirm that the compounds obtained were trialkoxytitanium fluorides, they were prepared also by treatment of the corresponding alkyl orthotitanates with acetyl fluoride according to the scheme:

$$Ti(OR)_4 + CH_3COF \rightarrow Ti(OR)_3F + CH_3COOR$$

This reaction for the preparation of alkoxyfluoro-derivatives of other elements was studied earlier by A. Ia. Iakubovich, S. P. Makarov, and V. A. Ginsburg [2].

EXPERIMENTAL

Preparation of diethoxyfluorostibine (I) from triethoxystibine and antimony trifluoride. Triethoxystibine was prepared according to the directions of Meerwein [3]. A mixture of 72.1 g of triethoxystibine (b. p. 101° at 17 mm, 76° at 4 mm) and 17.15 g of antimony trifluoride was heated, with stirring, at 140-150° with a reflux condenser for 7 hrs. As a result a homogeneous, crystalline mass with m. p. 60-70° was formed; the product was the double compound $Sb(OC_2H_5)_3 \cdot 3Sb(OC_2H_5)_2F$.

Found %: Sb 51.37; F 7.49. $C_{18}H_{45}O_9F_3Sb_4$. Calculated %: Sb 51.32; F 6.01.

On subsequent distillation of the substance in vacuo two fractions were obtained; the first had b. p. 72-77° at 2.5-3.5 mm, and its analysis corresponded to triethoxystibine.

Found %: Sb 47.24, 47.65. $C_6H_{15}O_3Sb$. Calculated %: Sb 47.42.

The second fraction had b. p. 164-166° (7 mm) and m. p. 49-52° after two-fold distillation and consisted of (I).

Found %: Sb 52.63, 53.28; F 7.44, 7.68; OC_2H_5 39.11, 39.39. $C_4H_{10}O_2FSb$. Calculated %: Sb 52.76; F 8.24; OC_2H_5 39.0.

The yield of (I), calculated on the basis of the triethoxystibine entering into the reaction, amounted to 77%. (I) was a very hygroscopic, colorless, crystalline substance, soluble in benzene, alcohol, or acetone (all anhydrous).

Preparation of diisopropoxyfluorostibine (II) from triisopropoxystibine and antimony trifluoride. A mixture of 19.7 g of $Sb(iso\text{-}OC_3H_7)_3$ [3] (b. p. 80-81° at 3.5 mm) and 4 g of SbF_3 was heated, with stirring, at 120-140° with a reflux condenser for 5 hrs. There was obtained a crystalline substance with m. p. about 40°, consisting of the double compound $Sb(iso\text{-}OC_3H_7)_3 \cdot 3Sb(iso\text{-}OC_3H_7)_2F$.

Found %: Sb 45.63. $C_{27}H_{63}O_9F_3Sb_4$. Calculated %: Sb 45.36.

When this compound was heated in vacuo, it decomposed, as a result of which triisopropoxystibine and (II) were formed. After distillation there was a certain amount of antimony trifluoride in the residue.

Both these esters distilled together at 68-72° (2-3 mm). Crystals of (II) could be obtained from the distillate on cooling.

Found %: Sb 46.17, 46.12; iso-OC_3H_7 46.26; F 7.19. $C_6H_{14}O_2FSb$. Calculated %: Sb 47; iso-OC_3H_7 45.66; F 7.34.

The yield of (II) was about 20%, calculated on the basis of the triisopropoxystibine entering into the reaction. (II) was a colorless, crystalline substance with m. p. 55°, very hygroscopic, readily soluble in alcohol or benzene (both anhydrous), and less soluble in acetone.

Preparation of triethoxytitanium fluoride (III). a) From ethyl orthotitanate and antimony trifluoride. Ethyl orthotitanate was prepared according to published directions [4]. A mixture of 15.75 g of $Ti(OC_2H_5)_4$ (b. p. 145° at 8.5 mm) and 4.118 g of SbF_3 was heated at 120-130° with stirring for 3 hrs. There was obtained a homogeneous, crystalline mass of the double compound $Sb(OC_2H_5)_3 \cdot 3Ti(OC_2H_5)_3F$, m. p. 82°.

Found %: Sb 15.08. $C_{24}H_{60}O_{12}SbF_3Ti_3$. Calculated %: Sb 14.12.

On subsequent distillation of this compound in vacuo, two fractions were obtained. The first fraction, having b. p. 62-64° (2 mm), consisted of triethoxystibine.

Found %: Sb 47.33. $C_6H_{15}O_3Sb$. Calculated %: Sb 47.42.

The yield, calculated on the basis of the double compound taken for distillation, was nearly quantitative.

The second fraction, which had b. p. 162-163° (2 mm) and m. p. 75-78°, was (III).

Found %: Ti 24.22, 23.15; OC_2H_5 67.05; F 9.38. $C_6H_{15}O_3FTi$. Calculated %: Ti 23.73; OC_2H_5 66.86; F 9.41.

The yield was 52.3%, calculated on the basis of the double compound taken for distillation. Triethoxytitanium fluoride (III) is a colorless, crystalline, very hygroscopic substance, readily soluble in benzene, ether (both absolute), alcohol, or acetone (both anhydrous); it dissolves better on heating.

b) From ethyl orthotitanate and acetyl fluoride. A mixture of 9.1 g of $Ti(OC_2H_5)_4$ and 2.5 g of CH_3COF was heated about 8 hrs in a sealed tube in a boiling water bath.

When the tube was opened, no acetyl fluoride was found. On distillation two fractions were obtained; the first had b. p. 77° and amounted to 1.5 g (ethyl acetate), whereas the second had b. p. 162-164° (2 mm) after two-fold distillation and corresponded to (III). Yield 6.2 g (85.5%).

Preparation of triisopropoxytitanium fluoride (IV) from isopropyl orthotitanate and antimony trifluoride. A mixture of 12.54 g of isopropyl orthotitanate (b. p. 93° at 6 mm) [4] and 2.63 g of SbF_3 was heated at 120-140° with stirring for 6 hrs. As a result a white, crystalline substance having the composition $Sb(iso\text{-}OC_3H_7) \cdot 3Ti(iso\text{-}OC_3H_7)_3F$ was obtained.

Found %: Sb 11.91. $C_{36}H_{84}O_{12}F_3Sb$. Calculated %: Sb 11.82.

On distillation in vacuo of 74 g of this compound, two fractions were obtained; the first had b. p. 67-74° (2.5 mm) and corresponded to triisopropoxystibine, whereas the second, distilled at 140-150° (6 mm) and solidified to a crystalline substance with m. p. 83-85°. The yield of (IV) was 30%, calculated on the basis of the double compound taken for distillation.

Found %: Ti 19.91, 19.17. $C_9H_{21}O_3FTi$. Calculated %: Ti 19.64.

Triisopropoxytitanium fluoride (IV) is a colorless, crystalline, very hygroscopic substance, readily soluble in benzene or ethyl alcohol (both anhydrous); in anhydrous acetone it dissolves better on heating.

Preparation of tributoxytitanium fluoride (V). a) From butyl orthotitanate and antimony trifluoride. A mixture of 30 g of $Ti(OC_4H_9)_4$ (b. p. 164-166° at 1.5 mm) [4] and 5.26 g of SbF_3 was heated at 130-160° for 6 hrs with stirring. A homogeneous liquid was obtained. On distillation of the reaction mass (32.32 g) in vacuo, two fractions were obtained after several distillations; the first (5.74 g), which had b. p. 121-124° (2 mm), corresponded to $Sb(OC_4H_9)_3$.

Found %: Sb 35.77. $C_{12}H_{27}O_3Sb$. Calculated %: Sb 35.73.

The yield was 62.5%, calculated on the basis of the liquid taken for distillation.

The second fraction, which had b. p. 175-180° (2 mm) (m. p. 45-48°), corresponded to (V).

Found %: Ti 16.42; OC_4H_9 76.8; F 7.04. $C_{12}H_{27}O_3FTi$. Calculated %: Ti 16.75; OC_4H_9 76.6; F 6.65.

The yield was 30.0%, calculated on the basis of the liquid taken for distillation. The product was a colorless, crystalline, very hygroscopic substance, readily soluble in anhydrous benzene; in alcohol and acetone (both anhydrous) it dissolved better on mild heating.

b) From butyl orthotitanate and acetyl fluoride. A mixture of 17 g of $Ti(OC_4H_9)_4$ and 3.1 g of CH_3COF was heated about 8 hrs in a sealed tube in a boiling water bath. A homogeneous liquid was obtained.

On distillation of the reaction liquid, two fractions were obtained; the first (5.2 g), which had b. p. 123-124°, was butyl acetate, whereas the second, which had b. p. 199-200° (3.5 mm), corresponded to (V). Yield 9.8 g (68.9%).

SUMMARY

1. It has been established that dialkoxyfluorostibines are obtained in the reaction of antimony trifluoride with trialkoxystibines.

2. Trialkoxytitanium fluorides and the corresponding trialkoxystibines have been isolated in the reaction of alkyl orthotitanates with antimony trifluoride.

3. It has been shown that this reaction proceeds through intermediate double compounds of the types $Sb(OR)_3 \cdot 3Sb(OR)_2F$ and $Sb(OR)_3 \cdot Ti(OR)_3F$, which decompose with the formation of dialkoxyfluorostibines and trialkoxytitanium fluorides.

4. It has been established that alkoxyfluoro-derivatives of titanium may be obtained also through the reaction of alkyl orthotitanates with acetyl fluoride.

Certain alkoxymonofluoro-derivatives of titanium and of trivalent antimony, which are not described in the literature, have been prepared.

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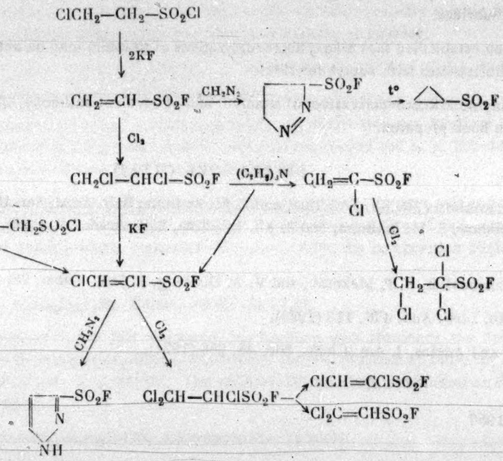
INVESTIGATION OF A SERIES OF ORGANIC SULFUR COMPOUNDS

IV. SYNTHESIS OF β-CHLOROETHANESULFONYL CHLORIDE

B. M. Gladshtein, I. P. Kuliulin, and L. Z. Soborovskii

β-Chloroethanesulfonyl chloride, as was shown earlier [1, 2], is an essential starting material in the synthesis of fluoroanhydrides of sulfonic acids of the ethane, ethylene, cyclopropane, pyrazoline, and pyrazole series. The reaction which was carried out – that of potassium fluoride with halogenated ethanesulfonyl chlorides and fluorides – made it possible to accomplish a direct transition from the stated compounds to sulfonyl fluorides of the olefin series, several more of which were synthesized in accordance with the scheme.

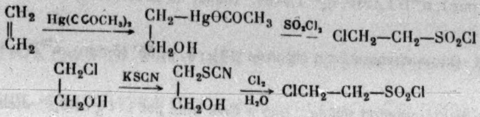

ClCH₂—CH₂—SO₂Cl
2KF
CH₂=CH—SO₂F
CH₂N₂
—SO₂F
N
N
t°
—SO₂F
Cl₂
CH₂Cl—CHCl—SO₂F
(C₂H₅)₃N
CH₂=C—SO₂F
Cl
Cl₂CH—CH₂SO₂Cl
KF
Cl₂
Cl
CH₂—C—SO₂F
Cl
Cl
ClCH=CH—SO₂F
CH₂N₂
Cl₂
—SO₂F
N
NH
Cl₂CH—CHClSO₂F—
ClCH=CClSO₂F
Cl₂C=CHSO₂F

Thus the availability both of ethylenesulfonyl fluoride itself and of substances synthesized on the basis thereof is determined by the availability of the original β-chloroethanesulfonyl chloride.

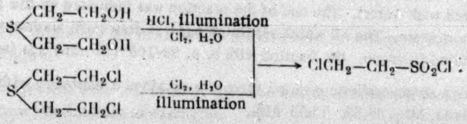
The methods of synthesis of β-chloroethanesulfonyl chloride described in the literature are based on the action of phosphorus pentachloride on salts of isethionic acid, which, in turn, are obtained either by the addition of a bisulfite to ethylene oxide [3] or by the hydrolysis of carbyl sulfate [4]. Patents were issued [5] on the preparation of β-chloroethanesulfonyl chloride according to the scheme:

$$ClCH_2—CH_2Cl \xrightarrow{Na_2SO_3} ClCH_2—CH_2SO_2ONa \xrightarrow{PCl_5} ClCH_2—CH_2SO_2Cl$$

Kohler [6] showed that β-chloroethanesulfonyl chloride is formed also on heating ethane-1,2-disulfonyl chloride. Other authors obtained β-chloroethanesulfonyl chloride in 62.7% yield through the oxidative chlorination of β-chloroethyl thiocyanate, formed from 1,2-dichloroethane and ammonium thiocyanate in an ethanol medium [7]. Attempts to synthesize β-chloroethanesulfonyl chloride according to the schemes given below were unsuccessful.



Positive results were obtained by us in the study of the following processes:



Experiment showed that the thiodiglycol, on chlorination in a concentrated hydrochloric acid medium, is converted to β-chloroethanesulfonyl chloride, with a yield greater than 50%. The importance of illumination, especially in the second half of the process, should be emphasized. Carrying this reaction out in the dark caused the yield of β-chloroethanesulfonyl chloride to fall to 5%.

In the oxidative chlorination of thiodiglycol there are formed together with β-chloroethanesulfonyl chloride, various chlorine-substituted hydrocarbons, of which pentachloroethane and symmetrical tetrachloroethane were isolated.

The described process of conversion of thiodiglycol to β-chloroethanesulfonyl chloride goes through an intermediate stage of formation of β,β'-dichlorodiethyl sulfide. The correctness of this is confirmed by the fact that β,β'-dichlorodiethyl sulfide itself, as we found, gives a satisfactory yield of β-chloroethanesulfonyl chloride when chlorinated in an aqueous medium with illumination.

Thus the reaction of oxidative chlorination of aliphatic [8] and cyclic sulfides [9], applied to thiodiglycol and β,β'-dichlorodiethyl sulfide, provides a convenient preparative method for the synthesis of β-chloroethanesulfonyl chloride.

The development of this method made it possible to combine sulfides of the aliphatic series, thiodiglycol, and β,β'-dichlorodiethyl sulfide by direct transitions with β-chloroethanesulfonyl chloride, ethylenesulfonyl fluoride, and other substances synthesized on the basis of the last series of conversions described by us earlier [1, 2].

EXPERIMENTAL

Chlorination of thiodiglycol. 50 g of thiodiglycol was stirred with 360 ml of hydrochloric acid (d 1.19) and a slow current of chlorine was passed into the mixture for 3 hrs at 65-70°. Then the mixture was cooled to 20° and illuminated by a lamp (400 w), and a vigorous current of chlorine was passed into the mixture. The reaction temperature was 50-55°. At the end of the reaction (which was indicated by the passage of chlorine through the mixture) the oil which separated out was drawn off, dried with calcium chloride, and distilled in vacuo. The following fractions were obtained: the first, having b. p. 33-92° (20 mm), and the second, having b. p. 92-102° (20 mm). On repeated distillation these fractions were isolated from the first:

B. p. 146-147° (759 mm), $n^{15}D$ 1.4928, d_4^{25} 1.5942 and b. p. 160-162° (759 mm), $n^{20}D$ 1.5022, d_4^{25} 1.6601.

Literature data for 1,1,2,2-tetrachloroethane: b. p. 146.2° [10], $n^{15}D$ 1.4967 [11], d_4^{25} 1.5881 [12].

Literature data for pentachloroethane: b. p. 161.9° [10], $n^{15}D$ 1.5054 [11], d_4^{25} 1.6712 [12].

Thus the first fraction contains pentachloroethane and symmetrical tetrachloroethane.

The isolation and identification of other chlorine-substituted ethanes having a lower degree of chlorination will be carried out in the future.

On distillation of the second fraction (35 g), β-chloroethanesulfonyl chloride was obtained (yield 52.5%).

B. p. 196-199° (751 mm), $n^{20}D$ 1.4918, d_4^{20} 1.5487. Found: M 163.6, MR_D 30.53. $C_2H_4O_2SCl_2$. Calculated: M 163.03, MR_D 30.1.

Literature data for β-chloroethanesulfonyl chloride [13]: b. p. 68° (5 mm), $n^{20}D$ 1.4920, d_4^{20} 1.555, MR_D 30.72.

Chlorination of β,β'-dichlorodiethyl sulfide. Into a flask were put 177 g of β,β'-dichlorodiethyl sulfide [b. p. 117-118° (20 mm)] and 1 liter of water and, with vigorous stirring and illumination by a lamp (200 w), a current of chlorine was passed into the mixture at such a rate as to insure its complete absorption. The temperature of the mixture reached 40-50° within 1 hr and was maintained at that level throughout the reaction (at first the mixture had to be cooled with water). The end of the reaction was indicated by the appearance of a faint, yellowish-green tint in the mixture. The oil which separated out was drawn off, washed with water, dried with calcium chloride, and distilled in vacuo; the fraction with b. p. 93-106° (20 mm) was isolated.*

By repeated distillation at atmospheric pressure there was obtained a substance with b. p. 198-204° (735 mm), $n^{20}D$ 1.4898, d_4^{20} 1.5434, MR_D 30.63. Yield 51%.

SUMMARY

The synthesis of β-chloroethanesulfonyl chloride by the oxidative chlorination of thiodiglycol (in a hydrochloric acid medium) or β, β'-dichlorodiethyl sulfide (in an aqueous medium) with illumination has been described.

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* Pentachloroethane and symmetrical tetrachloroethane were isolated also from the lower fraction, as described in the preceding experiment.

** Original Russian pagination. See C. B. translation.

INVESTIGATION IN THE FIELD OF ALKANESULFONIC ACIDS

XVIII. CHLORINATION OF ALKANESULFONIC ACID TOLUIDIDES

A. G. Kostsova and N. T. Borisova

Alkanesulfonic acid toluidides are described in the literature as antipyretics and antineuralgics [1]; chlorinated toluidides are unknown.

The purpose of the present work was to study the chlorination of alkanesulfonic acid o- and p-toluidides, using ethane- and butanesulfotoluidides as examples.

The reaction was carried out under the conditions described by us for the anilides of the stated sulfonic acids [2]. The reaction temperature and time of chlorination were varied; the rate at which chlorine was passed in remained constant in all experiments.

As our experiments showed, the yields of chlorination products sharply decrease in the presence of ZnO; change of temperature from 0 to 40° has little effect, although somewhat better results are observed at reduced temperatures; increase in the amount of solvent decreases the yields of products. On chlorination of the p-toluidides, mainly chloro-p-toluidides are formed at first, together with a negligible quantity of tetrachloro-p-toluidides, of which only ethanesulfotetrachloro-p-toluidide was isolated in pure form and characterized; butanesulfotetrachloro-p-toluidide was isolated in the form of a heavy, viscous mass, which could not be crystallized and purified. On increase of the chlorination time the yields of chloro-p-toluidides decrease, whereas those of tetrachlorotoluidides increase somewhat.

On chlorination of o-toluidides there are formed only chloro-o-toluidides, the quantity of which sharply decreases as the chlorination time increases. Tetrachloro-o-toluidides were not isolated.

The position of the chlorine in chloro-p-toluidides was proved by their hydrolysis to 3-chloro-p-toluidine, which was identified through its acetyl derivative.

For this purpose the chloro-o-toluidides were hydrolyzed and the resulting chloro-o-toluidine was then acetylated, but the data obtained were not sufficiently conclusive, since N-acetyl-5-chloro-o-toluidine and N-acetyl-4-chloro-o-toluidine have very similar constants. However, one argument in favor of the presence of 5-chloro-o-toluidine is the fact that many reactions carried out by us with toluidines showed that the stronger orienting substituent in these compounds is the alkanesulfonamido group and not the methyl; this argument is supported by the chlorination of the p-toluidide.

Chloro-o-toluidides are colorless, crystalline compounds, whereas chloro-p-toluidides are usually isolated in the form of heavy yellow oils, which distill in vacuo without decomposition and crystallize on standing or on cooling. Both of these and the others dissolve in organic solvents, and also in dilute alkali, from which they are precipitated on acidification; they are insoluble in water. By treatment in ether solution with metallic sodium, the sodium salt of ethanesulfochloro-o-toluidide was obtained. The acetyl derivatives of ethane- and butanesulfochloro-o-toluidides were obtained by treatment with acetic anhydride.

Tetrachloro-p-toluidides differ sharply in their properties from chlorotoluidides, in that they are insoluble in the cold in alcohol, ether, or dilute alkali, do not form salts with metallic sodium, are not alkylated, and are not acylated. These properties of tetrachloro-p-toluidides, so unusual for N-arylamides, are obviously due to steric hindrances resulting from the presence of two chlorine atoms in the ortho-position with respect to the NH

TABLE 1

Name of compound	Melting point	Content (in %)					
		N		Cl		S	
		found	calc.	found	calc.	found	calc.
Ethanesulfo-3-chloro-p-toluidide $C_9H_{12}O_2NSCl$	44—46°	5.92	5.99	15.22	15.20	13.63	13.70
Ethanesulfotetrachloro-p-toluidide $C_9H_9O_2NSCl_4$	140—142	4.17	4.15	41.73	42.10	9.78	9.49
Butanesulfo-3-chloro-p-toluidide $C_{11}H_{16}O_2NSCl$	38—40	5.10	5.35	13.46	13.54	12.08	12.22
Ethanesulfo-5-chloro-o-toluidide $C_9H_{12}O_2NSCl$	92—94	6.09	6.00	15.70	15.20	13.30	13.70
Butanesulfo-5-chloro-o-toluidide $C_{11}H_{16}O_2NSCl$	113—114	5.25	5.35	13.59	13.54	12.12	12.22
Sodium salt of ethanesulfo-5-chloro-o-toluidide $C_9H_{11}O_2NSClNa$	—	5.40	5.47	—	—	—	—
Ethanesulfo-N-acetyl-5-chloro-o-toluidide $C_{11}H_{14}O_3NSCl$	108—109	5.40	5.14	—	—	—	—
Butanesulfo-N-acetyl-5-chloro-o-toluidide $C_{13}H_{18}O_3NSCl$	71	4.33	4.81	—	—	—	—

group. A list of the compounds obtained, their constants, and analytical data are given in Table 1.

EXPERIMENTAL

Chlorination of ethane- and butanesulfonic acid p-toluidides. Into a solution of the p-toluidide in CCl_4 was passed a stream of chlorine gas, dried with sulfuric acid, at a rate of 3 ml/sec. At the end of the chlorination the reaction mixture was left until the next day; the CCl_4 was then distilled off or evaporated, and from the remaining viscous, yellow oil the reaction products — chlorotoluidides and tetrachlorotoluidides — were isolated by two methods.

1. The oil was treated with 5% alkali. During this treatment the tetrachlorotoluidide did not dissolve, but, in the case of ethanesulfo-p-toluidide, separated out in the form of a finely crystalline precipitate and in the case of butanesulfo-p-toluidide, precipitated in the form of a grayish, viscous mass; chloro-p-toluidides dissolved in the alkali, which in this case became quite dark. Since chlorination by-products apparently dissolved in the alkali along with the chlorotoluidide, only a very insignificant quantity of the chlorotoluidide could be isolated from the alkaline solution on acidification.

2. On treatment of the oil with alcohol the tetrachlorotoluidide, which is insoluble in cold alcohol, precipitated, whereas the chlorotoluidide passed into alcoholic solution, the alcohol was driven off in a water bath, and the residual chlorotoluidide distilled in vacuo at 180-190° (5 mm) for the ethane- and at 185-195° (4 mm) for the butanesulfo-derivative in the form of a viscous light-yellow oil, which crystallized on cooling. The chloro-p-toluidides were recrystallized from aqueous alcohol, and ethanesulfotetrachloro-p-toluidide, from hot alcohol; the tetrachloro-p-toluidide of butanesulfonic acid could not be purified and crystallized. We chlorinated butanesulfonic acid p-toluidide also in other solvents, for instance, ether, benzine, nitrobenzene, and glacial acetic acid, but were not able to obtain the crystalline tetrachlorotoluidide. The results of certain experiments in the chlorination of ethane- and butanesulfonic acid p-toluidides are given in Table 2.

Chlorination of ethane- and butanesulfonic acid o-toluidides. The chlorination was carried out as in the preceding case. In this case the crystalline chloro-o-toluidide precipitated within 5-8 min; it was filtered out, but after its removal the filtrate still contained a yellow oil, from which the crystalline tetrachloro-o-toluidide could not be isolated. The results of certain experiments in the chlorination of ethane- and butanesulfonic acid o-toluidides are given in Table 3.

The sodium salt of ethanesulfonic acid chloro-o-toluidide was prepared by the method described by us earlier [3]. From 2 g of the chloro-o-toluidide 1.4 g (67.3%) of the salt was obtained. The latter was a very

TABLE 2

Initial quantity of o-toluidide (in g)	Quantity of CCl_4 (in ml)	Time of passage of Cl_2 (in min)	Reaction temperature	Reaction products isolated (in %)	
				chloro-toluidide	tetrachloro-toluidide
Ethanesulfo-p-toluidide					
5	40	90	0–3°	25.6	37.2
5 (+ ZnO)	40	90	0–3	—	3.0
2.5	15	45	30–8	34.1	17.3
2.5	15	15	15–10	78.5	Traces
Butanesulfo-p-toluidide					
6	25	90	2–7	21.7	—
6	25	120	2–7	14.5	—
6	25	20	0–3	64.4	—

TABLE 3

Initial quantity of o-toluidide (in g)	Quantity of CCl_4 (in ml)	Time of passage of Cl_2 (in min)	Temperature	Chloro-o-toluidide isolated (in %)
Ethanesulfo-o-toluidide				
9	40	15	2–8°	66.5
5 (+ZnO)	25	8	2–8	48.5
4.5	25	14	30–18	53.1
Butanesulfo-o-toluidide				
5	20	15	20–0	75.0
5	20	30	20–0	59.7
5	20	15	40–15	67.0
5	20	30	38–16	56.8
5 (+ ZnO)	20	15	18–2	16.7

hygroscopic, amorphous, white powder. On acetylation of ethane- and butanesulfonic acid chloro-o-toluidides by the method described earlier [2], 1.24 g (69%) of the acetyl derivative was obtained from 1.6 g of ethanesulfochloro-o-toluidide and 3.4 g of acetic anhydride, and 0.9 g (66.6%) of the acetyl derivative was obtained from 1.2 g of butanesulfochloro-o-toluidide and 3.2 g of acetic anhydride. The acetyl derivatives were recrystallized from aqueous alcohol.

Hydrolysis of chlorotoluidides. The hydrolysis was carried out with sulfuric acid (1 : 1) for several hours until addition of water to a test sample ceased to cause precipitation. 1 g of the substance and 10 ml of acid were taken. At the end of the reaction the mixture was alkalized, the separated chlorotoluidine was extracted with ether, and the ether extract was dried with potash; then the ether was distilled off and the residual oil (chlorotoluidine) was treated with acetyl chloride. The resulting precipitate, after evaporation of excess acetyl chloride, was recrystallized from aqueous alcohol. On hydrolysis of ethane- and butanesulfonic acid chloro-p-toluidides and subsequent acetylation there was obtained N-acetyl-3-chloro-p-toluidine, m. p. 114-117°; according to literature data, m. p. 118° [4]. On hydrolysis of ethane- and butanesulfonic acid chloro-o-toluidides there was obtained N-acetyl-5-chloro-o-toluidine, m. p. 138-139°; according to literature data, m. p. 140° [4]. Analysis of the acetyl derivatives of the chlorotoluidines for nitrogen gave satisfactory results.

SUMMARY

1. The chlorination of ethane- and butanesulfonic acid o- and p-toluidides under various conditions has been studied.

2. Ethane- and butanesulfonic acid chloro-o- and p-toluidides, as well as ethanesulfonic acid tetrachloro-p-toluidide, have been isolated and characterized.

3. The sodium salt of ethanesulfonic acid chloro-o-toluidide and the N-acetyl derivatives of ethane- and butanesulfonic acid chloro-o-toluidides have been prepared and characterized.

4. The structure of chloro-p-toluidides has been proved by the reaction of hydrolysis.

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** In Russian.

ALKYLATION OVER AN ALUMINOSILICATE CATALYST ACTIVATED BY GASEOUS HYDROGEN CHLORIDE

I. ALKYLATION OF BENZENE BY ALKYL CHLORIDES

I. F. Radzevenchuk

In 1943 it was observed that gumbrin in the presence of hydrogen chloride can catalyze the alkylation reaction at 70° [1]. At that time this reaction seemed improbable and was not investigated in detail. During the last few years reactions over aluminosilicates have come into wide use. The reactions of polymerization and depolymerization [2], catalytic cracking [3], and alkylation [4] have been studied. Therefore, we have attempted to carry out reactions between benzene and alkyl halides under the conditions characteristic of reactions with $AlCl_3$.

In the presence of a natural aluminosilicate (gumbrin), dried at 160-170° to constant weight, and gaseous hydrogen chloride at 70-76°, the alkylation of benzene by isopropyl chloride, n-butyl chloride, and isobutyl chloride was carried out. As the result of a series of experiments alkylbenzenes were obtained in the following yields: propylbenzenes, 70%, and butylbenzenes, 50 and 70%, respectively (yields calculated on the basis of alkyl halide).

As preliminary experiments showed, an essential point for insuring the success of the alkylation at 70-76° is the drying of the gumbrin at 160° and its treatment with hydrogen chloride in a medium consisting of the alkylating reagents. The gumbrin had to be dried until the interstitial water was removed. For this it was heated to constant weight in a thermostat at 160-170°; in this case it lost 14.2% water. Drying at 310-320 and 425-450° gave only an insignificant increase in the percentage of water removed (0.4%), and the activity of the catalyst was not increased. At 500° the gumbrin lost 23.5% water and its activity diminished. It may be assumed that at this temperature partial decomposition of the structural hydroxyls takes place with formation of the "anhydrous modification" of montmorillonite [5]. The structure of the silicate and hydrargillite layers changes, and therefore the activity of the gumbrin falls. It is generally known that montmorillonites can absorb liquids. Thus, when ethylene glycol was absorbed by montmorillonite, the glycol molecules formed double layers among the blocks of the montmorillonte lattice [6, 7]. It is possible that after removal of the interstitial water the mixture of benzene and alkyl chloride took its place; thus the reagents closely approached the active centers of the aluminosilicate and formed complexes with it, and a catalytic reaction became more probable. However, as was stated earlier, thermal treatment of the gumbrin is not in itself sufficient to make the alkylation reaction go at 70°. A second, no less important condition is the passage of a current of dry hydrogen chloride through the benzene-alkyl halide mixture. The alkylation reaction did not take place with gumbrin dried at 160°, but passage of a current of dry hydrogen chloride through a suspension of the clay in the reagents for 15 min was enough to make the reaction begin. Propylbenzenes were formed in 40% yield. Increase in the time of passage of HCl to 3 hrs decreased the yield of alkylbenzenes. As was ascertained by a series of experiments, it is expedient to pass the HCl through for 1-1.5 hr. In the literature [8, 9] there is a statement that treatment of Al_2O_3 by gaseous hydrogen chloride at 300-400° substantially heightens its catalytic properties in isomerization reactions. The authors explain the increase in the activity of the Al_2O_3 by the presence on its surface of bound chloride ions resulting from the reaction of surface hydroxyl groups with HCl. The increase in the activity of dry gumbrin on treatment with gaseous HCl in the alkylation experiments also can be explained by taking into account the structure of montmorillonite clays and the presence of Si, isomorphically substituted for Al [10]. The yield of alkylbenzenes was affected also by the fact that the clay and hydrogen chloride gas were added not to benzene, but to a benzene-alkyl halide mixture. It is possible that, as was proved for $AlCl_3$ [11], the catalysis here is ionic in character.

The activity acquired by the clay is retained for some time. After the alkylation reaction was carried out, the clay layer had catalytic properties. New portions of alkyl halide and benzene were successfully alkylated with it.

The process of alkylation is accompanied by isomerization of the alkyl halides taken into the reaction. For instance, in the alkylation of isobutyl chloride, di-tert-butylbenzene was obtained. Such isomerization also accompanies the reaction with $AlCl_3$, as is generally known, and is observed also in vapor-phase alkylation over an aluminosilicate catalyst [4]. The molar ratio of alkyl halide to benzene in all experiments was equal to 0.2 : 1. In the reaction with $AlCl_3$ [12] such a ratio was stated to be most expedient for obtaining monoalkyl derivatives.

EXPERIMENTAL

A three-neck flask with stirrer was charged with 30-60 g of gumbrin dried at 160-170°. One-third of the benzene and alkyl halide, taken into the reaction, was added. The alkyl halides were prepared from the corresponding alcohols by treatment with conc. HCl in the presence of $ZnCl_2$ [13]. Both the benzene and the alkyl halides were carefully dried over $CaCl_2$ and distilled before the reaction. Their constants corresponded to literature data. The benzene-alkyl halide mixture was heated in a water bath to 60-70°; a bent tube reaching to the bottom was inserted in the second neck of the flask, and a strong current of dry HCl was passed through the tube. The third neck of the flask was coupled to a bulb condenser. The end of the condenser was closed by a calcium-chloride drying tube. During the first 7 min the HCl was absorbed by the clay, and after that it passed out through the drying tube.

Mechanical stirring was not used in this step. After 1-1.5 hrs the HCl current was stopped, the HCl delivery tube was taken out, and a dropping funnel was put in its place. The temperature of the bath was raised to 70°. The mechanical stirrer was turned on, and the rest of the benzene-alkyl halide mixture was added dropwise through the dropping funnel during 1-1.5 hr. The progress of the reaction was marked by the evolution of HCl. After addition of the mixture the temperature was raised to 76-78°. Heating and stirring were continued for 3-8 hrs, until the evolution of HCl ceased. After settling, the upper hydrocarbon layer was decanted from the blackened clay, washed with 10% NaOH and dried over $CaCl_2$. The clay was transferred to a flask, and the adsorbed hydrocarbons were removed by steam distillation. The hydrocarbons obtained were dried and distilled. In all cases one distillation through a column was sufficient for the isolation of pure alkylbenzenes. Therefore we obtained purer individual alkylation products than with $AlCl_3$ prepared according to published data [14].

Alkylation of benzene by isopropyl chloride. The experiments were conducted with a molar ratio of benzene to isopropyl chloride, equal to 1 : 0.22. The effects on the yield of alkylbenzenes of the temperature at which the clay was dried, the time of passage of hydrogen chloride, the order and time of addition of the reagents, and the temperature and duration of the reaction were investigated. Better results were obtained in the case where the clay was dried at 160-170° (loss of water, 14.2%). Time of passage of hydrogen chloride, 1 hr (at 60°). Time of addition of the rest of the benzene-isopropyl chloride mixture, 75 min. Temperature 70-76°. Reaction time 7 hrs. Yield of propylbenzenes, 70% (these were 87% isopropylbenzene). After the first distillation through a column the isopropylbenzene (first fraction) had the following constants:

B. p. 151-152.5°, $n^{20}D$ 1.14915, d_4^{20} 0.8615, MR_D 40.40; calc. 40.20. M 120, 123; calc. 120.2.

The second fraction, obtained in the quantity 6%, distilled at 190-192° and had $n^{20}D$ 1.4918; it obviously consisted of diisopropylbenzene with a slight admixture of isopropylbenzene. The residue had $n^{20}D$ 1.4960.

Alkylation of benzene by isobutyl chloride. The isobutyl chloride had b. p. 68-70°. The ratio of benzene to isobutyl chloride was equal to 1 : 0.20. 25 g of clay per 100 g of benzene was taken. The remaining conditions were the same as in the preceding experiment. The yield of alkylation products amounted to 70% (based on the isobutyl chloride taken). After distillation through a column two fractions were isolated. The residue (18%) was also distilled through a column. The first fraction (10%) had b. p. 166-169° and $n^{20}D$ 1.4908. Obviously this was tert-butylbenzene (b. p. 169°, $n^{20}D$ 1.4908 [15]). The second fraction (42%) had the constants:

B. p. 169-170°, $n^{20}D$ 1.4920, d_4^{20} 0.8656, MR_D 44.9; calc. 44.8. M 135.4; calc. 134.1. Literature data for isobutylbenzene: b. p. 170°, $n^{20}D$ 1.4928, d_4^{20} 0.8673 [15].

On distillation a fraction with b. p. 190° was isolated from the residue in the quantity 7%. Crystals separated out from this and from the residue on cooling. After several recrystallizations from alcohol they had m. p. 78°. Among the butylbenzenes the only solid substance is di-tert-butylbenzene, m. p. 77.8° [15].

The formation of di-tert-butylbenzene indicates that the original alkyl halide was isomerized.

Alkylation of benzene by n-butyl chloride. Alkylation under the conditions of the preceding experiments gave only 50% alkylbenzenes. This low yield is possibly due to the lesser activity of butyl chloride. By distillation through a column a fraction (38%) with b. p. 168-171°, $n^{18}D$ 1.4900, and a residue (12%) were isolated. Melting point of the diacetylamino derivative, 192°. M 131; calc. 134.1. Obviously this fraction consisted of sec-butylbenzene. The residue had $n^{20}D$ 1.4940 and M 146 and was probably a mixture of polybutylbenzenes.

SUMMARY

The alkylation of benzene by isopropyl chloride, isobutyl chloride, and butyl chloride has been carried out in the presence of gumbrin, dried at 160°, and gaseous hydrogen chloride. Reaction temperature 70-76°. It has been established that the principal reaction products are monoalkylbenzenes.

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DEPENDENCE OF THE YIELD AND THE QUALITY OF BENZENESULFONYL CHLORIDE ON THE EXCESS OF CHLOROSULFONIC ACID AND ADDITION OF SODIUM SALTS

L. I. Levina, S. N. Patrakova, and D. A. Patrushev

A number of authors [1-4] have been concerned with the problem of raising the yield and improving the quality of commercial sulfonyl chlorides.

No indications are to be found in the literature concerning the effect of additions of salts of alkali metals on the quality of the sulfonyl chlorides produced. In the present study we investigated the effect of the excess of chlorosulfonic acid and of additions of salts of sodium on the yield and the quality of benzenesulfonyl chloride.

As shown by B. Iu. Iasnitskii [5] and A. A. Spryskov [6, 7], the reaction of formation of benzenesulfonyl chloride is a reversible one and, consequently, the yield of benzenesulfonyl chloride should be raised by increased excess of chlorosulfonic acid, which fact is confirmed by experimental data (see Table). At the same time, the quality of benzenesulfonyl chloride (the content of sulfones as admixtures to it) to an insignificant degree does depend on the excess of chlorosulfonic acid.

Dependence of Yield and Quality of Benzenesulfonyl Chloride on the Ratio of Benzene and Chlorosulfonic Acid and Additions of Sodium Salts

Molar ratio of benzene to chlorosulfonic acid	Yield of commercial benzenesulfonyl chloride (%)			Analysis of benzenesulfonyl chloride (in %)								
				acidity			content of sulfones			content of benzenesulfonyl chloride		
	no addition of salts	addition of Na_2SO_4	addition of NaCl	no addition of salts	addition of Na_2SO_4	addition of NaCl	no addition of salts	addition of Na_2SO_4	addition of NaCl	no addition of salts	addition of Na_2SO_4	addition of NaCl
1 : 2.5	78.2	—	—	0.11	—	—	4.9	—	—	94.8	—	—
1 : 3.0	83.1	—	—	0.17	—	—	4.6	—	—	95.2	—	—
1 : 5.0	87.8	—	—	0.80	—	—	4.0	—	—	95.0	—	—
1 : 2.5	—	64.2	—	—	0.09	—	—	1.68	—	—	98.0	—
1 : 3.0	—	78.6	—	—	0.05	—	—	1.03	—	—	98.0	—
1 : 5.0	—	80.0	—	—	0.50	—	—	0.20	—	—	99.3	—
1 : 2.5	—	—	71.8	—	—	0.25	—	—	3.10	—	—	96.3
1 : 3.0	—	—	82.0	—	—	0.10	—	—	2.07	—	—	97.8
1 : 5.0	—	—	86.9	—	—	0.43	—	—	1.80	—	—	97.1

It follows from the above table that the addition of sodium sulfate leads to a decline of the yield of benzenesulfonyl chloride with a small excess of chlorosulfonic acid (0.5 mole over the stoichiometric ratio). With excess of chlorosulfonic acid equal to 1 mole or more, the addition of sodium sulfate does not affect the yield but does raise the quality of benzenesulfonyl chloride by lowering the content of sulfones from 4.0-4.9 to 0.2-1.68%. A similar effect on the process of chlorosulfonation is exerted by the addition of sodium chloride to the original chlorosulfonic acid. The lowering of the amount of sulfone admixture may be explained by the formation of sodium benzenesulfonate, which is an inhibitor of the formation of sulfones in sulfonation of benzene by a high percentage oleum [8].

EXPERIMENTAL*

The experiments were run in a round-bottomed flask provided with a reflux condenser, a stirrer, a dropping funnel, a thermometer and a tube for leading off the hydrogen chloride. To twice-distilled chlorosulfonic acid (containing dried sodium chloride or sulfate) there was added from the dropping funnel over 6 hrs the required amount of benzene. The reaction was run at 20-26°. The content of the principal substance and of sulfones was determined in the resulting benzenesulfonyl chloride by saponification with N solution of sodium hydroxide. The acidity of the product was determined by means of 0.1 N solution of sodium hydroxide.

SUMMARY

The yield of benzenesulfonyl chloride is raised from 78.2% to 87.8% by increase of the amount of chlorosulfonic acid from 2.5 to 5 moles per 1 mole of benzene. The lowering of the sulfone content is achieved by the addition of sodium sulfate or chloride to the original chlorosulfonic acid.

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ACETALS OF β,β-DIHALO SUBSTITUTED PROPIONALDEHYDES

T. V. Protopopova and A. P. Skoldinov

In our previous communication [1] there was described the application of derivatives of β,β-dihalo substituted propionaldehydes with the general formula $CHX_2CH_2CHBr(OCOCH_3)$ (I, X = Cl or Br) for the synthesis of various heterocyclic compounds. The acetals of these aldehydes were also of interest since they could serve as starting materials for the preparation of the thus far unknown free β,β-dihalo substituted propionaldehydes and β-halo substituted acroleins. Only dimethyl acetal of β,β-dichloropropionaldehyde [2] had been described among such acetals up to the present time.

$$CHX_2CH_2CHBr(OCOCH_3) \longrightarrow CHX_2CH_2CH(OR)_2 \rightleftarrows CHX_2CH_2CHX'(OR)$$

$$\begin{array}{lll} \text{(I) } X = Cl,\ Br & \text{(II) } X = Cl,\ Br & \text{(III) a) } X = X' = Cl,\ R = CH_3 \\ & \phantom{\text{(II) }} R = CH_3,\ C_2H_5,\ n\text{-}C_3H_7,\ n\text{-}C_4H_9 & \phantom{\text{(III) }}\text{b) } X = X' = Cl,\ R = C_2H_5 \\ & & \phantom{\text{(III) }}\text{c) } X = Br,\ X' = Cl,\ R = CH_3 \\ & & \phantom{\text{(III) }}\text{d) } X = X' = Br,\ R = CH_3 \end{array}$$

By the action of an appropriate alcohol on (I) we prepared in satisfactory yields a series of acetals (II) which were colorless liquids, which possessed characteristic odors and were distillable in vacuum without decomposition; they were stable to storage in the cold. These acetals were relatively stable in respect to dilute acids; however, treatment with acids under more drastic conditions led to cleavage of hydrogen halides and formation of polymeric products. The results of action of basic reagents on acetals (II) will be disclosed in a future communication.

Acetals (II) are transformed into the corresponding 1,1,3-trihalo-3-alkoxypropanes (III)* by cleavage of an alkyl chloride in the reaction with phosphorus pentachloride or thionyl chloride in an inert solvent or without a solvent. One of the halogen atoms in these compounds is quite mobile – it is readily hydrolyzed even in the cold by water, which fact permits one to titrate quantitatively the compounds of type (III) by mercurometric methods. Such properties of compounds (III) agree completely with their structure of alkyl α,γ,γ-trihalopropyl ethers.

The preparation of (III d) could not be accomplished by the reaction of substance (II, X = Br) with phosphorus pentabromide owing to the brominating action of the latter; (III d) was prepared by treatment of (III c) with hydrogen bromide [3]. As the result of reaction of (III) with alcohols one obtains compounds (II) again, which fact was demonstrated in the example of transformation of (III a) and (III b) into the corresponding acetals.

(II) and (III), just like other functional derivatives of malonodialdehyde, are capable of condensation with nitrogenous compounds analogous to condensations previously described for (I). For example, in the reaction of such compounds with hydrazine, there is formed pyrazole, with hydroxylamine there is formed isoxazole [1], with urea there is formed 2-hydroxypyrimidine, with thiourea there is obtained 2-mercaptopyrimidine [4], with guanidine there is formed 2-aminopyrimidine [2, 4, 5], etc. There is no need to cite these reactions in the experimental section, but one should note that the reactivity of the presently described compounds declines in the series (III) > (I) > (II), which fact is connected with the relative ease of liberation of the aldehyde group in compounds of this type.

EXPERIMENTAL

Preparation of the Acetals

A mixture of 0.1 mole of 1,1-dihalo-3-bromo-3-acetoxypropane and 1.5-2.0 moles of the corresponding alcohol, after standing for four days at room temperature, were poured into a cooled solution of sodium bicarbonate and the separated oil was extracted with ether; the residue after the removal of ether was fractionated in vacuo. In this manner there were prepared the following acetals:

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* The transformation of (II) into (III) proceeds especially smoothly under the action of thionyl chloride in the presence of catalytic amounts of tertiary amines.

Dimethyl acetal of β,β-dichloropropionaldehyde (yield 70%):

B. p. 67-68° (18.5 mm), $n^{20}D$ 1.4400, d_4^{20} 1.1954, MR_D 38.09; calc. 38.30.

Literature data [2]: b. p. 70° (18 mm).

Diethyl acetal of β,β-dichloropropionaldehyde (yield 80%).

B. p. 65-66° (6 mm), $n^{20}D$ 1.4380, d_4^{20} 1.1118, MR_D 47.50; calc. 47.55. Found %: C 41.67, 41.48; H 6.85, 6.91; Cl 35.08, 34.96. $C_7H_{14}O_2Cl_2$. Calculated %: C 41.79; H 6.96; Cl 35.32.

Di-n-propyl acetal of β,β-dichloropropionaldehyde (yield 55%).

B. p. 77-78° (2-2.5 mm), $n^{20}D$ 1.4428, d_4^{20} 1.0725, MR_D 56.59; calc. 56.76. Found %: C 47.35, 47.24; H 7.38, 7.87. $C_9H_{18}O_2Cl_2$. Calculated %: C 47.16; H 7.86.

Di-n-butyl acetal of β,β-dichloropropionaldehyde (yield 75%).

B. p. 108-109° (3 mm), $n^{20}D$ 1.4460, d_4^{20} 1.0358, MR_D 66.18; calc. 66.02. Found %: C 51.66, 51.35; H 8.63, 8.50. $C_{11}H_{22}O_2Cl_2$. Calculated %: C 51.36; H 8.56.

Dimethyl acetal of β,β-dibromopropionaldehyde (yield 82%).

B. p. 59-60° (2 mm), $n^{20}D$ 1.4912, d_4^{20} 1.7194, MR_D 44.17; calc. 44.10. Found %: C 22.54, 22.67; H 4.02, 4.00; Br 66.25, 61.46. $C_5H_{10}O_2Br_2$. Calculated %: C 22.90; H 3.81; Br 61.00.

Diethyl acetal of β,β-dibromopropionaldehyde (yield 62%).

B. p. 70-71° (1.5 mm), $n^{20}D$ 1.4755, d_4^{20} 1.5211, MR_D 53.63; calc. 53.34. Found %: C 29.28, 29.25; H 5.02, 5.03; Br 54.85, 54.68. $C_7H_{14}O_2Br_2$. Calculated %: C 28.95; H 4.82; Br 55.17.

Di-n-propyl acetal of β,β-dibromopropionaldehyde (yield 60%).

B. p. 97-98° (1.5 mm), $n^{20}D$ 1.4740, d_4^{20} 1.4228, MR_D 62.77; calc. 62.58. Found %: C 33.97, 33.26; H 5.70, 5.76; Br 50.17, 50.07. $C_9H_{18}O_2Br_2$. Calculated %: C 33.96; H 5.66; Br 50.31.

Di-n-butyl acetal of β,β-dibromopropionaldehyde (yield 50%).

B. p. 120-121° (2 mm), $n^{20}D$ 1.4728, d_4^{20} 1.3469, MR_D 71.87; calc. 71.81. Found %: C 38.32, 38.33; H 6.38, 6.29; Br 46.15, 46.01. $C_{11}H_{22}O_2Br_2$. Calculated %: C 38.15; H 6.35; Br 46.24.

Preparation of α,γ,γ-Trihalopropyl Alkyl Ethers

1,1,3-Trichloro-3-methoxypropane. To a mixture of 18.1 g (0.104 mole) of dimethyl acetal of β,β-dichloropropionaldehyde and 12.5 g (0.105 mole) of distilled thionyl chloride, preheated to 65°, there was added one drop of pyridine; after the evolution of sulfur dioxide became weaker, the mixture was heated until the gas evolution ceased completely by raising the bath temperature gradually to 90-95°. After fractionation in vacuum, with protection from atmospheric moisture, there was obtained 13.8 g (78%) of the product.

B. p. 45.5-48° (7 mm), $n^{20}D$ 1.4630, d_4^{20} 1.3201, MR_D 37.07; calc. 36.92. Found %: Cl^- 20.03, 20.01; Cl_{total} 60.36, 60.24. $C_4H_7OCl_3$. Calculated %: Cl^- 20.00; Cl_{total} 60.00.

1,1,3-Trichloro-3-ethoxypropane. To a suspension of 9.1 g (0.043 mole) of phosphorus pentachloride in 15 ml of dry carbon tetrachloride there was rapidly added 8.6 g (0.042 mole) of diethyl acetal of β,β-dichloropropionaldehyde. After completion of the exothermic reaction, the mixture was refluxed for 20 min longer and was then fractionated in vacuum; there was obtained 7.3 g (91%) of a fraction with b. p. 49-53° (4 mm). The substance was distilled twice.

B. p. 38.5-40° (1.5 mm), $n^{20}D$ 1.4578, d_4^{20} 1.2543, MR_D 41.67; calc. 41.53. Found %: C 31.73, 31.70; H 4.77, 4.80; Cl^- 18.22, 18.47. $C_5H_9OCl_3$. Calculated %: C 31.41; H 4.71; Cl^- 18.53.

1,1-Dibromo-3-chloro-3-methoxypropane was prepared analogously (yield 90%).

B.p. 53.5-55° (1.5 mm), $n^{20}D$ 1.5165. Found %: Cl^- 13.21, 13.18. $CHBr_2CH_2CHCl(OCH_3)$. Calculated %: Cl^- 13.32.

1,1,3-Tribromo-3-methoxypropane. 1,1-Dibromo-3-chloro-3-methoxypropane (15.7 g; 0.059 mole) was saturated with dry hydrogen bromide; the excess of hydrogen bromide was removed by blowing with dry air and the residue was fractionated in vacuum. There was obtained 9.4 g (50%) of a liquid which fumed strongly in air.

B. p. 83-85° (2 mm), $n^{20}D$ 1.5495, d_4^{20} 2.1231, MR_D 46.33; calc. 45.61. Found %: Br^- 25.39, 25.10; Br_{total} 76.67, 76.73. $CHBr_2CH_2CHBrOCH_3$. Calculated %: Br^- 25.72; Br_{total} 77.17.

Reaction of 1,1,3-trichloro-3-ethoxypropane with alcohol. A mixture of 4 g of 1,1,3-trichloro-3-ethoxypropane and 17 ml of anhydrous ethyl alcohol was kept for 20 hrs at room temperature, after which it was poured into a solution of sodium bicarbonate and the separated oil was extracted with ether. After vacuum fractionation there was obtained 3.8 g (90%) of diethyl acetal of β,β-dichloropropionaldehyde; b. p. 64-66° (6 mm), $n^{20}D$ 1.4355.

Dimethyl acetal of β,β-dichloropionaldehyde was prepared analogously (74%); b. p. 66-66.5° (18.5 mm), $n^{23}D$ 1.4360.

SUMMARY

1. A series of acetals with general formula $CHX_2CH_2CH(OR)_2$, where X = Cl or Br, R = CH_3, C_2H_5, n-C_3H_7 or n-C_4H_9, was prepared and some of the properties of these compounds were studied.

2. Alkyl α, γ,γ-trihaloalkyl ethers with the general formula $CHX_2CH_2CHX'(OR)$ were prepared by the reaction of the acetals with phosphorus pentachloride or thionyl chloride.

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HETEROCYCLIC COMPOUNDS

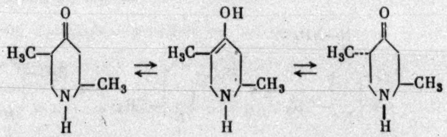
LXII. STEREOCHEMISTRY OF 1-ACYL-2,5-DIMETHYL-4-PIPERIDONES

I. N. Nazarov, N. S. Prostakov, and N. N. Mikheeva

Recently the 2,5-dimethyl-4-piperidones [2] preparable by the reaction of propenyl isopropenyl ketone [2] with ammonia or primary amines, have been used widely in our laboratory for the synthesis of various 4-piperidols and their esters. Among the latter are the propionates of stereoisomeric 1,2,5-trimethyl-4-phenyl-4-piperidols – Promedol, Isopromedol and α-Promedol – prepared in our laboratory [3]. Promedol (γ-isomer) turned out to be a highly active analgesic which exceeded morphine in activity by about 2-3-fold. Isopromedol (β-isomer) turned out to be more active than Promedol by 2-fold. However, the most active pain-relieving properties were possessed by α-Promedol, which exceeded the activity of Isopromedol by a factor of 2. The dependence of physiological activity on the spatial structure was also established for the propionates of stereoisomeric 1,3-dimethyl-4-phenyl-4-piperidols (α-Prodin and β-Prodin [4]).

We supposed that during the study of stereochemistry of 4-piperidones we might obtain data which would permit us to approach the establishment of the steric or spatial structure of 4-phenyl-4-piperidols and their esters.

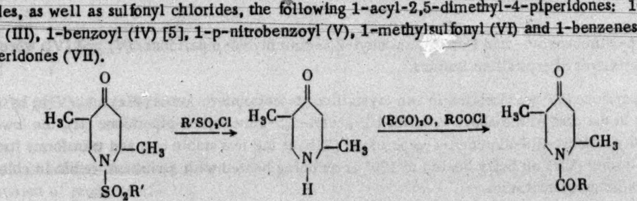
2,5-Dimethyl-4-piperidone (I) can exist in two stereoisomeric forms (cis and trans). Up to the present time these stereoisomeric forms had not been isolated which fact is evidently connected with the ease of their mutual transformations.



(I) cis form (I) trans form

One may expect that in the series of 1-acyl-2,5-dimethyl-4-piperidones having an amide nitrogen with considerably reduced basic properties, the mutual transformations of the isomeric piperidones would not proceed with such facility and therefore it would be possible to isolate and to study the individual stereoisomers.

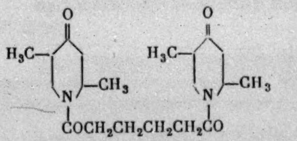
For this reason we prepared during the treatment of 2,5-dimethyl-4-piperidone (I) with acid anhydrides and acyl chlorides, as well as sulfonyl chlorides, the following 1-acyl-2,5-dimethyl-4-piperidones: 1-acetyl (II) [5], 1-propionyl (III), 1-benzoyl (IV) [5], 1-p-nitrobenzoyl (V), 1-methylsulfonyl (VI) and 1-benzenesulfo-2,5-dimethyl-4-piperidones (VII).



(I)

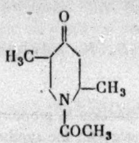
(VI), $R' = CH_3$; (VII), $R' = C_6H_5$; (II) $R = CH_3$; (III), $R = C_2H_5$; (IV), $R = C_6H_5$; (V), $R = p\text{-}NO_2C_6H_4$

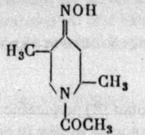
The diamide (VIII) was prepared in low yield by acylation of piperidone (I) with the chloride of adipic acid.

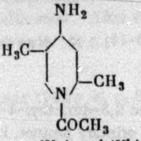

(VIII)

1-Acetyl-2,5-dimethyl-4-piperidone (II) was isolated in a crystalline (IIa) and a liquid state (IIb) in 1:1 ratio. The proportion of the crystalline and the liquid fractions depends on the method of treatment. By subjecting the liquid fraction to repeated distillation and by simply heating it to 150-160° it was possible to change this fraction totally into the crystalline isomer.

The crystalline and the liquid isomers form two different oximes (IXa) and (IXb), which after reduction with sodium in alcohol yielded two different 1-acetyl-2,5-dimethyl-4-aminopiperidines (Xa) and (Xb).

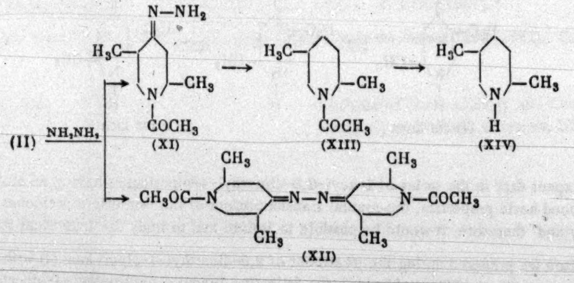

(IIa) and (IIb)


(IXa) and (IXb)


(Xa) and (Xb)

1-Benzoyl-2,5-dimethyl-4-piperidone (IV) was also isolated in fractions of crystalline and liquid form. Piperidones (II) and (IV) were hydrolyzed by 20% aqueous solution of sulfuric acid to the original 2,5-dimethyl-4-piperidone (I). An attempt to prepare hydrazones of both isomeric 1-acetyl-2,5-dimethyl-4-piperidones (IIa) and (IIb) failed to give the desired positive results. Both from the crystalline isomer (IIa) and from the liquid fraction containing mainly isomer (IIb) there was formed one and the same hydrazone (XI) which corresponded to the more stable stereoisomeric form of 1-acetyl-2,5-dimethyl-4-piperidone (IIa). The less stable form of piperidone (IIb) evidently isomerizes during the preparation of the hydrazone into the more stable form (IIa) under the influence of the alkaline medium. The preparation of hydrazone of 1-acetyl-2,5-dimethyl-4-piperidone is accompanied by the formation of a considerable amount of the azine (XII).

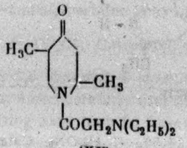
The hydrazone of 1-acetyl-2,5-dimethyl-4-piperidone (XI) was further reduced by the Kizhner method to 1-acetyl-2,5-dimethylpiperidine (XIII), which was deacetylated to 2,5-dimethylpiperidine (XIV).



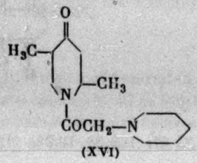
1-p-Nitrobenzoyl- and 1-methylsulfonyl-2,5-dimethyl-4-piperidones (V) and (VI) were prepared in the form of mixtures of crystalline isomers.

Piperidone (VI) was isolated in two crystalline stereoisomeric forms (VIa) and (VIb) by fractional crystallization. As in the case of the above-described 1-acetyl-2,5-dimethyl-4-piperidone (II), the lower melting isomer of 1-methylsulfonyl-2,5-dimethyl-4-piperidone (VIb) is the less stable one and transforms itself into the higher melting isomer (VIa) on being heated to 120° or on being heated with aluminum oxide in chloroform, the transformation being quantitative.

By acylation of 2,5-dimethyl-4-piperidone (I) with chloroacetyl chloride and subsequent treatment of the resulting 1-chloroacetyl-2,5-dimethyl-4-piperidone with diethylamine, as well as piperidine, there were prepared 1-diethylaminoacetyl- (XV) and 1-N-piperidylacetyl-2,5-dimethyl-4-piperidone (XVI).



(XV)



(XVI)

The hydrochloride of piperidone (XVI) produces a comparatively weak anesthetic action in 0.5% solution.

EXPERIMENTAL

2,5-Dimethyl-4-piperidone (I). For preparation of (I) we used the mixture of 2-methyl-1,4-hexadien-3-one, 2-methyl-5-methoxy-1-hexen-3-one and 2-methyl-1,5-dimethoxy-3-hexanone (b. p. 71° at 16 mm, 62° at 4.5 mm), which was heated with aqueous ammonia solution, or with ammonium acetate at the boiling point of methanol if the reaction was run in a methanol solution, or at 90-95° if methanol was not employed. In the latter case, the reaction mixture was stirred energetically. The reaction of cyclization with the aqueous ammonia solution was run in a hermetically closed vessel; in other cases it was run in the usual round-bottomed flask with a reflux condenser or in a three-necked flask provided with a stirrer and a reflux condenser. Methanol was distilled off after the completion of heating, slight vacuum being used for the distillation, and then the mixture was treated, with cooling, with 18% hydrochloric acid until it became acid to Congo red. The unreacted ketones were extracted with ether. The residual aqueous solution was evaporated and treated with potassium hydroxide with cooling, until the amine layer formed. The amines were extracted 5-8 times with ether. The ethereal extracts were dried with calcined sodium sulfate or potassium carbonate after which the reaction products were distilled twice in vacuo. The 2,5-dimethyl-4-piperidone, after the two distillations, had b. p. 76-78° (9 mm), 66° (6 mm), $n^{20}D$ 1.4676.

2,5-Dimethyl-4-piperidone acetate, formed in the reaction of cyclization by means of ammonium acetate, formed long colorless needle-like crystals with m. p. 92-94°.

Found %: N 7.46, 7.48. $C_9H_{17}O_3N$. Calculated %: N 7.49.

In the following table there are shown the yields of 2,5-dimethyl-4-piperidone after running the cyclization reaction: 1) with aqueous ammonia solution with an 8% excess of the latter; 2) with ammonium acetate (30% excess) in aqueous methanol; 3) under analogous conditions but without methyl alcohol.

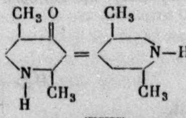
Yields of 2,5-Dimethyl-4-piperidone

	Mixtures of ketones (g)	Ammonia (in g)	Acetic acid (g)	Water (in ml)	Methyl alcohol (in ml)	Duration of heating (in hrs)	Am't of 2,5-dimethyl-4-piperidone obtained (g)	Recovery of ketones (g)	2,5-Dimethyl-4-piperidone yield based on ketone mixture (in %)	
									ketones used for reaction	reacted ketones (conversion)
1	310	36	—	115	150	6	70	59.4	28	34.7
2	500	70	248	385	500	7	167.5	69.3	41.6	48.1
3	500	70	248	710	—	12	157	28	39.1	41.4

Note. The average molecular weight of the mixture of the starting ketones was taken to be 158.

Under all the conditions described above for the preparation of 2,5-dimethyl-4-piperidone there was formed a considerable amount of products with high boiling points along with a tarry residue. From the fractions boiling considerably above the piperidone there was isolated the product of its condensation – 2,5-dimethyl-3-(2',5'-

dimethyl-4'-piperidylidene)-4-piperidone (XVII), in the form of a viscous green liquid with b. p. 130-134° (2.5 mm), $n^{20}D$ 1.4990. Its hydrochloride melted at 225° (from alcohol).



(XVII)

Found %: C 70.76, 71.31; H 9.58, 10.28; N 11.82, 11.50. $C_{14}H_{24}ON_2$. Calculated %: C 71.19; H 10.17; N 11.86.

1-Acetyl-2,5-dimethyl-4-piperidone (II). To 123.5 g of freshly distilled 2,5-dimethyl-4-piperidone there was added, with cooling and stirring, 146 g of acetic anhydride. The mixture was then heated for 8 hrs at 70-80°. It turned dark and became viscous. After the distillation of the acetic anhydride residue, the remaining material was twice distilled in vacuo. There was obtained 144.5 g of substance (II) with b. p. 134-136° (3 mm), $n^{20}D$1.4900.

Found %: N 7.98, 8.21, 7.96, 8.03. $C_9H_{15}O_2N$. Calculated %: N 8.28.

The distilled piperidone crystallized in part. There was obtained 74 g of colorless crystals with m. p. 60-61°, which corresponded to piperidone (IIa).

Found %: N 8.10, 8.50. $C_9H_{15}O_2N$. Calculated %: N 8.28.

After the separation of the crystalline piperidone (IIa) there remained 70 g of the liquid isomer of the piperidone (IIb). 2 g of it was heated for 45 min at 150-160°. The mixture crystallized immediately after being cooled. There was isolated 0.7 g of piperidone (IIa) with m. p. 60-61°.

Hydrolysis of 1-acetyl-2,5-dimethyl-4-piperidone. 1-Acetyl-2,5-dimethyl-4-piperidone (IIa; 4.3 g) with m. p. 60-61° and 20 g of 20% sulfuric acid were refluxed for 5 hrs. The reaction mixture was carefully treated with sodium hydroxide. The upper layer of organic bases was taken up in ether and dried. After vacuum distillation there was obtained 2.7 g of 2,5-dimethyl-4-piperidone (I) with b. p. 71.5° (8.5 mm), $n^{21}D$ 1.4670.

Oxime of 1-acetyl-2,5-dimethyl-4-piperidone (IXa) and (IXb). a) To a solution of 6 g of 1-acetyl-2,5-dimethyl-4-piperidone (IIa) with m. p. 60-61° and 3 g of hydroxylamine hydrochloride in 10 ml of water there was added 6 g of sodium bicarbonate. The resulting precipitate (6.5 g) of the oxime of 1-acetyl-2,5-dimethyl-4-piperidone (IXa) melted at 159-160°, after recrystallization from alcohol.

Found %: N 15.02, 15.32. $C_9H_{16}O_2N_2$. Calculated %: N 15.22.

b) Analogously, from 2 g of 1-acetyl-2,5-dimethyl-4-piperidone (IIb), 2 g of sodium bicarbonate, 1 g of hydroxylamine hydrochloride and 10 ml of water, the oxime (IXb) (1.2 g) with m. p. 179-181° (from alcohol)was prepared.

Found %: N 15.18, 15.36. $C_9H_{16}O_2N_2$. Calculated %: N 15.22.

1-Acetyl-2,5-dimethyl-4-aminopiperidine (Xa) and (Xb). a) To a boiling solution of 4 g of oxime (IXa) (m. p. 159-160°) in 50 ml of anhydrous alcohol there was added, in small pieces but quite rapidly, 5 g of metallic sodium. The last portion of sodium was dissolved by heating. The excess alcohol was distilled in slight vacuum and the residue was dissolved in water and repeatedly extracted with ether. After distillation of ether from the ethereal extract which had been dried with sodium sulfate, there remained 2 g of a liquid which was distilled in vacuum. There were obtained the following fractions: 1st, b. p. 45-53° (3 mm), 0.3 g, $n^{20}D$ 1.4791; and 2nd, b. p. 138-140° (3 mm), 0.6 g, $n^{20}D$ 1.4950.

From the second fraction there was obtained 0.5 g of hydrochloride of 1-acetyl-2,5-dimethyl-4-aminopiperidine (Xa) with m. p. 273-275° (from anhydrous alcohol).

Found %: N 13.36, 13.05. $C_9H_{19}ON_2Cl$. Calculated %: N 13.56.

b) The reduction of oxime of 1-acetyl-2,5-dimethyl-4-piperidone (IXb) (m. p. 179-181°) was run analogously; 1 g of the oxime, 1.3 g of sodium and 20 ml of anhydrous alcohol being used. Hydrogen chloride was passed into the ethereal solution of the base, after separation from the drying agent. An oil formed, which crystallized after addition of alcohol. After recrystallization from alcohol there was obtained 0.2 g of the hydrochloride of 1-acetyl-2,5-dimethyl-4-aminopiperidine (Xb) with m. p. 328-331°.

Found %: N 13.87. $C_9H_{19}ON_2Cl$. Calculated %: N 13.56.

Hydrazone of 1-acetyl-2,5-dimethyl-4-piperidone (XI). To 40 g of 1-acetyl-2,5-dimethyl-4-piperidone (IIa) (m. p. 60-61°) there was added carefully with shaking and cooling 35 ml of 85% hydrazine hydrate. The mixture was heated on a boiling water bath for 30 min. The excess hydrazine hydrate was distilled off and the residue was twice distilled in vacuo. There was obtained 32 g of the hydrazone of 1-acetyl-2,5-dimethyl-4-piperidone (XI) with b. p. 162-164° (3 mm), $n^{20}D$ 1.5338.

Found %: N 22.48, 22.70. $C_9H_{17}ON_3$. Calculated %: N 22.95.

After distillation of hydrazone (XI) there remained a residue from which there was isolated the azine of 1-acetyl-2,5-dimethyl-4-piperidone (XII) with b. p. 225-230° (3 mm).

Found %: N 17.04, 16.80. $C_{18}H_{30}O_2N_4$. Calculated %: N 16.77.

1-Acetyl-2,5-dimethylpiperidine (XIII) and 2,5-dimethylpiperidine (XIV). 30 g of freshly distilled hydrazone of 1-acetyl-2,5-dimethyl-4-piperidone (XI) and 7 g of fused potassium hydroxide were heated in a flask, provided with a distilling condenser, up to 120°. Immediately a decomposition of the hydrazone began accompanied by a violent evolution of nitrogen and distillation of a liquid. The vapor temperature reached 130-200°. Additional 23 g of fused potassium hydroxide was added in small portions during the course of the decomposition. The distilled substance was dissolved in absolute ether, dried with potassium carbonate and distilled. There were obtained the following fractions: 1st, b. p. 137-138° (4.7 g), $n^{20}D$ 1.4440, and 2nd, b. p. 88-91° (3 mm) 5.9 g, $n^{20}D$ 1.4742.

The first fraction was a volatile liquid with a sharp amine odor, which was 2,5-dimethylpiperidine (XIV). Its hydrochloride, after two recrystallizations from acetone, melted at 196-197°.

Found %: Cl 23.74, 23.67. $C_7H_{16}NCl$. Calculated %: Cl 23.74.

The second fraction – a liquid with unpleasant odor – was 1-acetyl-2,5-dimethylpiperidine (XIII).

Found %: N 8.70, 9.04. $C_9H_{17}ON$. Calculated %: N 9.03.

2 g of 1-acetyl-2,5-dimethylpiperidine (XIII) was heated with 5 g of potassium hydroxide at about 200°. There distilled 1 g of a liquid, which yielded the above-described hydrochloride of 2,5-dimethylpiperidine by the conventional treatment.

1-Propionyl-2,5-dimethyl-4-piperidone (III). To a solution of 60 g of freshly distilled 2,5-dimethyl-4-piperidone in 100 ml of anhydrous benzene there was added, with cooling and stirring, 22 g of propionyl chloride dissolved in 50 ml of benzene. The reaction mixture was stirred for 2 hrs at room temperature. The resulting precipitate of the hydrochloride of the original piperidone was filtered off and washed with benzene. From the mother liquor there was isolated by a vacuum distillation 36.5 g of 1-propionyl-2,5-dimethyl-4-piperidone (III) with b. p. 123-126° (2.5 mm).

Found %: N 7.69, 7.79. $C_{10}H_{17}O_2N$. Calculated %: N 7.65.

From the resulting mixture of stereoisomeric 1-propionyl-2,5-dimethyl-4-piperidones (III) there was isolated the oxime with m. p. 103-104.5° (from aqueous alcohol).

Found %: N 14.07, 13.91. $C_{10}H_{18}O_2N_2$. Calculated %: N 14.14.

1-Benzoyl-2,5-dimethyl-4-piperidone (IV). To 150 g of freshly distilled 2,5-dimethyl-4-piperidone in 150 ml of benzene there was added with cooling and stirring a solution of 83 g of benzoyl chloride in 50 ml of benzene. The mixture was heated for 5 hrs at gentle reflux of benzene. The precipitate was filtered off and repeatedly washed on the filter with benzene and ether. There was obtained 65.4 g of the hydrochloride of 2,5-dimethyl-4-piperidone which was recrystallized from a mixture of acetone and alcohol. Thereby there was obtained at first 45.6 g of crystals with m. p. 143-145°, while from the mother liquors there were obtained in succession three precipitates of 6.5, 5.8 and 0.7 g, whose melting points depended on the temperature at which the samples were introduced into the melting point apparatus. If the sample were heated gradually from 20-30°, it melted just as the first isolated portion of the crystals at 143-145°; if the sample were introduced into the apparatus preheated to 120-130°, the sample melted instantly.

The solvent was distilled from the mother liquor remaining after the isolation of the hydrochloride of 2,5-dimethyl-4-piperidone. The residue, 170.5 g, was a viscous red liquid which was treated with heating by means of three portions of ether of 300 ml each. During the distillation of the substance extracted with ether, the distillation being made in vacuum, there was obtained 117.5 g of 1-benzoyl-2,5-dimethyl-4-piperidone (IV) in the form of a viscous liquid with b. p. 173° (3 mm), $n^{20}D$ 1.5480.

Found %: N 6.10, 6.10. $C_{14}H_{17}O_2N$. Calculated %: N 6.06.

The piperidone crystallized after addition of absolute ether and cooling.

The precipitate was filtered off and washed with ether. There was obtained 36 g of crystals with m. p. 60-67°, while from the mother liquor there was isolated further some 22.4 g of crystals with m. p. 58-63°. The first precipitate (36 g) was recrystallized from ether. There was obtained 27.3 g of one of the stereoisomeric forms of 1-benzoyl-2,5-dimethyl-4-piperidone with m. p. 65.5-67.5°.

Found %: N 6.53, 6.33. $C_{14}H_{17}O_2N$. Calculated %: N 6.06.

The oxime of this isomer melted at 172-173° (from alcohol).

After the isolation of crystalline fractions of the piperidone there remained an uncrystallizable oil substance which was a mixture of stereoisomeric 1-benzoyl-2,5-dimethyl-4-piperidones. From 3.8 g of this substance there was obtained 2.9 g of a mixture of oximes of stereoisomeric piperidones with m. p. 147-159° (from alcohol; one of the precipitates).

Found %: N 11.71, 11.39. $C_{14}H_{18}O_2N_2$. Calculated %: N 11.38.

In benzoylation of 2,5-dimethyl-4-piperidones under other conditions there were obtained the following results:

a) From 45 g of 2,5-dimethyl-4-piperidone and 42 ml of benzoyl chloride after heating to 90-95° for 4 hrs there was obtained 34 g of 1-benzoyl-2,5-dimethyl-4-piperidone and 12 g of the starting piperidone (I).

b) There was used 45 g of 2,5-dimethyl-4-piperidone, 60 g of sodium hydroxide dissolved in 105 ml of water and 84 g of benzoyl chloride. The reaction was run with cooling with ice water. There was obtained 53 g of 1-benzoyl-2,5-dimethyl-4-piperidone.

Hydrolysis of 1-benzoyl-2,5-dimethyl-4-piperidone. 2 g of 1-benzoyl-2,5-dimethyl-4-piperidone was heated for 10 hrs at 100° with 20 ml of 20% sulfuric acid. Benzoic acid was extracted with ether. From the aqueous solution, after an alkaline treatment and extraction with ether, there was isolated 1 g of a liquid, after the distillation of which in vacuo there was obtained 0.3 g of 2,5-dimethyl-4-piperidone (I) with b. p. 80° (9 mm), $n^{20}D$ 1.4665. Picrate (from alcohol), m. p. 167-168°.

1-p-Nitrobenzoyl-2,5-dimethyl-4-piperidone (V). 56 g of 2,5-dimethyl-4-piperidone, 41.2 g of p-nitrobenzoyl chloride (m. p. 73-74.5°) and 200 ml of anhydrous benzene were heated for 5 hrs at the boiling point of benzene. The hydrochloride of 2,5-dimethyl-4-piperidone was filtered off and washed with 100 ml of benzene. The precipitate which remained after the distillation of benzene was recrystallized from acetone. There was obtained 22 g of a mixture of stereoisomeric 1-p-nitrobenzoyl-2,5-dimethyl-4-piperidones with m. p. 128-138°. By repeated crystallization from acetone there was isolated one of the stereoisomeric 1-p-nitrobenzoyl-2,5-dimethyl-4-piperidones (V) with m. p. 144-146°.

Found %: N 10.20, 10.39. $C_{14}H_{16}O_4N_2$. Calculated %: N 10.14.

1-Methylsulfonyl-2,5-dimethyl-4-piperidone (VI). Methanesulfonyl chloride (18.2 g) dissolved in 25 ml of anhydrous benzene was added slowly with cooling and stirring to a solution of 32.5 g of 2,5-dimethyl-4-piperidone (I) in 100 ml of benzene. After stirring for 2 hrs at room temperature the precipitate of the hydrochloride of 2,5-dimethyl-4-piperidone (21.5 g) was filtered off and washed repeatedly with benzene. The solvent was distilled from the mother liquor under slight vacuum. There was obtained 35.2 g of a viscous light red oil. 2 g of this residue was subjected to a vacuum distillation. There was obtained 1.8 g of a substance with b. p. 130-136° (10 mm), which crystallized immediately in the receiver. After recrystallization from a mixture of acetone and ether there was isolated one of the stereoisomers of 1-methylsulfonyl-2,5-dimethyl-4-piperidones (VIa) with m. p. 98-100°.

Found %: N 7.15, 7.22. $C_8H_{15}O_3NS$. Calculated %: N 6.83.

To the remaining 33.2 g there was added 100 ml of absolute ether. The resulting precipitate was filtered off and washed with absolute ether. There was obtained 17.9 g of colorless crystals with m. p. 49-60°. From the mother liquor there were isolated two more precipitates of 4.4 g with 60-64° and 2.4 g with m. p. 58-65°. These were mixtures of stereoisomeric 1-methylsulfonyl-2,5-dimethyl-4-piperidones.

Analysis of precipitate with m. p. 49-60°.

Found %: N 6.68, 6.67. $C_8H_{15}O_3NS$. Calculated %: N 6.83.

The oxime obtained from the mixture of stereoisomeric 1-methylsulfonyl-2,5-dimethyl-4-piperidones melted at 151-155° (from alcohol).

Found %: N 13.15, 13.00. $C_8H_{16}O_3N_2S$. Calculated %: N 12.77.

1 g of the mixture of stereoisomeric piperidones (VI) with m. p. 49-60° was recrystallized twice from absolute ether. There was obtained 0.3 g of a second stereoisomeric form of 1-methylsulfonyl-2,5-dimethyl-4-piperidone (VIb) with m. p. 76-78°, which melted at 58-63° in a mixed melting point with the above-described isomer (VIa) with m. p. 98-100°.

Found %: N 6.90, 6.99. $C_8H_{15}O_3NS$. Calculated %: N 6.83.

The oxime of the lower melting isomer of 1-methylsulfonyl-2,5-dimethyl-4-piperidone melted at 168.5-170° (from aqueous acetone). The oxime of the high melting isomer of 1-methylsulfonyl-2,5-dimethyl-4-piperidone had m. p. 166-167° (from aqueous acetone). The mixed melting point of the two oximes of isomeric piperidone (VI) was 148-157°.

Isomerization of low melting isomer of 1-methylsulfonyl-2,5-dimethyl-4-piperidone (VIb) into the high-melting isomer (VIa). a) 1-Methylsulfonyl-2,5-dimethyl-4-piperidone (VIb; 0.1 g; m. p. 76-78°) was heated without a solvent for 1.5 hr at 100-120°. After addition of absolute ether there was isolated 0.07 g of crystals with m. p. 93-95°, which did not give a depression in mixed melting point with the high melting isomer of 1-methylsulfonyl-2,5-dimethyl-4-piperidone (VIa).

b) A solution of 0.2 g of 1-methylsulfonyl-2,5-dimethyl-4-piperidone (VIb) with m. p. 76-78° in 20 ml of dry chloroform was heated on a water bath with stirring for 2 hrs with 3 g of aluminum oxide. After distillation of chloroform and addition of ether, the residue crystallized. There was isolated 0.15 g of the high melting isomer of 1-methylsulfonyl-2,5-dimethyl-4-piperidone (VIa) with m. p. 96-98°.

c) 1.5 g of a mixture of stereoisomeric 1-methylsulfonyl-2,5-dimethyl-4-piperidones (VI) with m. p. 49-60° was heated without a solvent for 20 min at 120-130°. After addition of 2 ml of acetone there formed a precipitate which, after being washed with ether, was heated in acetone solution with activated carbon. There was obtained 0.52 g of crystals with m. p. 95-97°, which in mixed melting point with the above-described sample of 1-methylsulfonyl-2,5-dimethyl-4-piperidone (VIa) gave no depression.

1-Benzenesulfonyl-2,5-dimethyl-4-piperidone (VII). 2,5-Dimethyl-4-piperidone (17 g), 40 ml of a 12% aqueous solution of sodium hydroxide and 42 g of benzenesulfonyl chloride were heated for 8 hrs on a water bath with energetic stirring. A crystalline precipitate (25 g) formed on cooling; this was 1-benzenesulfonyl-2,5-dimethyl-4-piperidone with m. p. 124-126° (from anhydrous alcohol).

Found %: N 5.06, 5.10. $C_{13}H_{17}O_3NS$. Calculated %: N 5.24.

1,1'-Adipoylbis(2,5-dimethyl-4-piperidone)(VIII). 20 g of 2,5-dimethyl-4-piperidone and 7.6 g of the chloride of adipic acid, dissolved in 40 ml of benzene, were heated for 2.5 hrs at the boiling point of benzene. After distillation of benzene, the residue was dissolved in 20 ml of water, treated with sodium hydroxide and then with 200 ml of ether. After drying of the ethereal solution with sodium sulfate and distillation of the ether, there was obtained 23.4 g of an oily substance from which there was vacuum distilled 9 g of the initial 2,5-dimethyl-4-piperidone (I). The remaining viscous mass was treated, with heating, with 4 portions of ether, 30 ml each. From the combined ethereal extracts there formed, after cooling and partial removal of ether, a colorless precipitate (0.9 g) of 1,1'-adipoylbis(2,5-dimethyl-4-piperidone) with m.p. 104-108° (after washing with absolute ether).

Found %: N 7.46, 7.76. $C_{20}H_{32}O_4N_2$. Calculated %: N 7.69.

1-Diethylaminoacetyl-2,5-dimethyl-4-piperidone (XV). To a solution of 17 g of 2,5-dimethyl-4-piperidone in 2.5 ml of benzene there was added with cooling and stirring a solution of 22 ml of chloroacetyl chloride in 25 ml of benzene. The red homogeneous solution was heated for 5 hrs at the boiling point of benzene. Then, 30 ml of diethylamine was added and heating was continued for 4 hrs at the boiling point of the amine. The benzene and the excess diethylamine were distilled off in vacuo. The residue was dissolved in water and was treated with sodium carbonate until saturated. The reaction products were extracted with ether and were vacuum distilled after having been dried. There was obtained 14 g of 1-diethylaminoacetyl-2,5-dimethyl-4-piperidone, in the form of a viscous liquid with b. p. 145° (3 mm).

Found %: N 11.63, 11.56. $C_{13}H_{24}O_2N_2$. Calculated %: N 11.66.

There was also obtained 7.4 g of a substance boiling at 60-145° (3 mm) and a residue of 5.5 g which dissolved readily in hydrochloric acid.

1-N-Piperidylacetyl-2,5-dimethyl-4-piperidone (XVI). 2,5-Dimethyl-4-piperidone (22.7 g), 17 ml of chloroacetyl chloride and 50 ml of benzene were heated for 2 hrs at the boiling point of benzene. The excess chloroacetyl chloride and benzene were distilled off in vacuo. To the residue there was added 50 ml of benzene and 40 ml of freshly distilled piperidine. The mixture was heated for 4 hrs at 50-60°. The piperidine and benzene were distilled off in vacuo and the residue was dissolved in water and treated with sodium carbonate, after which an ether extraction was made.

After distillation of the reaction products in vacuum there was obtained 17.5 g of 1-N-piperdylacetyl-2,5-dimethyl-4-piperidone (XVI) in the form of a sirupy liquid with b. p. 136° (2.5 mm).

Found %: N 10.84, 10.78. $C_{14}H_{24}O_2N_2$. Calculated %: N 11.11.

1-N-Piperidylacetyl-2,5-dimethyl-4-piperidone hydrochloride melted at 205-207° after recrystallization from acetone.

Found %: N 9.81, 9.81. $C_{14}H_{25}O_2N_2Cl$. Calculated %: N 9.70.

SUMMARY

A series of 1-acyl-2,5-dimethyl-4-piperidones was prepared. Some of these were obtained in two geometrically isomeric forms (cis and trans). It was shown that one of the isomeric piperidones had less stability and isomerized relatively readily into the more stable form.

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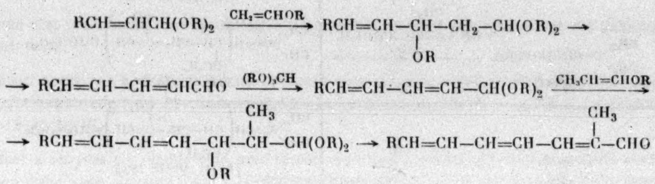
CONDENSATION OF ACETALS WITH 1-ETHOXYDIENES

A NEW METHOD OF SYNTHESIS OF POLYENE ALDEHYDES OF ISOPRENE TYPE

I. N. Nazarov and Zh. A. Krasnaia

Vinyl ethers have been successfully used in recent years for the synthesis of polyene aldehydes of the carotenoid series.

In the condensation of acetals with vinyl ethyl or propenyl ethyl ethers there are formed ether acetals which are then transformed into α, β-unsaturated aldehydes by the following scheme [1, 2]:



$$RCH{=}CHCH(OR)_2 \xrightarrow{CH_2=CHOR} RCH{=}CH{-}\underset{\displaystyle OR}{CH}{-}CH_2{-}CH(OR)_2 \rightarrow$$

$$\rightarrow RCH{=}CH{-}CH{=}CHCHO \xrightarrow{(RO)_3CH} RCH{=}CH{-}CH{=}CH{-}CH(OR)_2 \xrightarrow{CH_3CH=CHOR}$$

$$\rightarrow RCH{=}CH{-}CH{=}CH{-}\underset{\displaystyle OR}{CH}{-}\overset{\displaystyle CH_3}{CH}{-}CH(OR)_2 \rightarrow RCH{=}CH{-}CH{=}CH{-}CH{=}\overset{\displaystyle CH_3}{C}{-}CHO$$

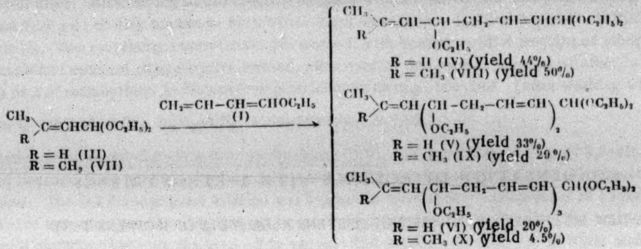
Use of vinyl ethyl and propenyl ethyl esters permits one to grow the polyene chain by two and three carbon atoms with introduction of one double bond.

We decided to use in the synthesis of polyene aldehydes the dienic ethers which had not been previously used for this purpose. For 1-alkoxydienes we selected 1-ethoxy-1,3-butadiene [3] (I) and ethoxyisoprene (3-methyl-1-ethoxy-1,3-butadiene) (II) which had been recently synthesized in our laboratory [4]. The use of ethoxyisoprene would permit one to lengthen the polyene chain by 5 carbon atoms at once, with introduction of 2 double bonds and a methyl group into the position necessary for the isoprenoids.

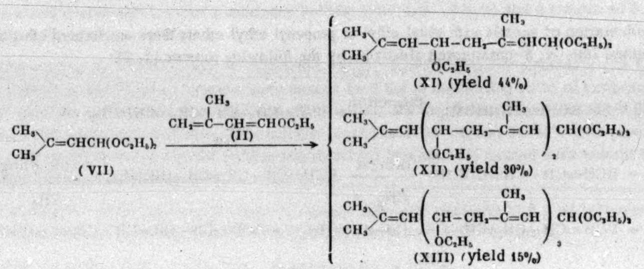
As expected, the condensation of acetals of α, β-unsaturated aldehydes with ethoxybutadiene and ethoxyisoprene proceeded readily under the influence of zinc chloride or boron trifluoride. The acetals add to ethoxybutadiene and ethoxyisoprene in 1,4-position; thereby are formed, in high yields, the corresponding α, β-unsaturated ether acetals, which are then smoothly converted, depending on the reaction conditions, to ether aldehydes and polyeneals.

In the reaction of the acetal of crotonaldehyde (III) with ethoxybutadiene (I), under the influence of boron trifluoride at the temperature of 0-5°, there was obtained in the total yield of 97% a mixture of the ether acetals (IV), (V) and (VI) (see diagram at top of following page).

Formation of ether acetal (V) is explained by the fact that the resulting, from the reaction, ether acetal (IV) is in turn added to a second molecule of ethoxybutadiene. Ether acetal (VI) is formed analogously from ether acetal (V) and ethoxybutadiene. From ether acetal (IV), isolated in pure state, and ethoxybutadiene there were obtained, in the presence of boron trifluoride ethereate, the ether acetals (V) and (VI) in yields of 38% and 36%, respectively. As the result of the condensation of the acetal of dimethylacrylaldehyde (VII) with ethoxybutadiene, under the influence of boron trifluoride ethereate at 0-5° or zinc chloride at 60-65°, there was obtained a mixture of ether acetals (VIII), (IX) and (X), in the total yield of 83.5%. In the condensation of ether acetal (VIII) with



ethoxybutadiene there were formed ether acetals (IX) and (X), in yields of 22.5 and 32%, respectively. Ethoxyisoprene (II) enters the reactions with the acetals even more readily than does ethoxybutadiene. In the reaction of acetal (VII) with ethoxyisoprene (II), under the influence of zinc chloride at room temperature, there was obtained in the total yield of 89% a mixture of ether acetals (XI), (XII) and (XIII).



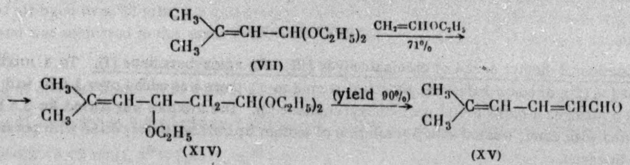
In the condensation of ether acetal (XI) with ethoxyisoprene under the same conditions there were formed ether acetals (XII) and (XIII) in yields of 41 and 25%, respectively.

The reactions of acetals with ethoxydienes, as shown by our experiments, do not proceed singularly: as the result of the reaction there is formed a mixture of ether acetals, which are the products of addition of one, two or three molecules of the ethoxydiene to the acetal. The formation of ether acetals with high molecular weight is explained by the fact that as the result of addition of the unsaturated acetal to ethoxydiene there is formed again an unsaturated ether acetal, which enters sufficiently readily into a reaction with a second molecule of the ethoxydiene, etc. In order that the main reaction products be ether acetals formed as the result of addition of one or two molecules of ethoxydiene to the acetal, it is necessary to use the excess of the acetal. The effect of the excess acetal (VII) on the yield of the resulting ether acetals is evident in the example of condensation of acetal (VII) with ethoxyisoprene (II) under the influence of zinc chloride (see Table below).

We also realized the condensation of acetal (VII) with vinyl ethyl ether. In this case we used equimolar amounts of the acetal (VII) and the vinyl ethyl ether, and nevertheless obtained only one ether acetal (XIV) in

Acetal (VII) (g)	Ethoxyisoprene (II) in g	Molar ratio (VII) : (II)	Ether acetal (VIII)		Ether acetal (IX)		High-boiling ether acetals and residue (in g)
			g	%	g	%	
9.9	7.0	1 : 1	2.2	13	1.5	12.6	4.9
14.0	6.6	1.5 : 1	5.5	35	3.2	28.5	2.8
23.2	6.6	2.5 : 1	7.0	44	2.9	26.0	2.5
37.2	6.6	4 : 1	7.5	47	3.8	34.0	2.0

the yield of 71%, this being converted then into 2-methyl-2,4-hexadien-6-al (XV).



CH₃
CH₃
C=CH–CH(OC₂H₅)₂
CH₂=CHOC₂H₅
71%
(VII)
C=CH–CH–CH₂–CH(OC₂H₅)₂
OC₂H₅
(XIV)
(yield 90%)
C=CH–CH=CHCHO
(XV)

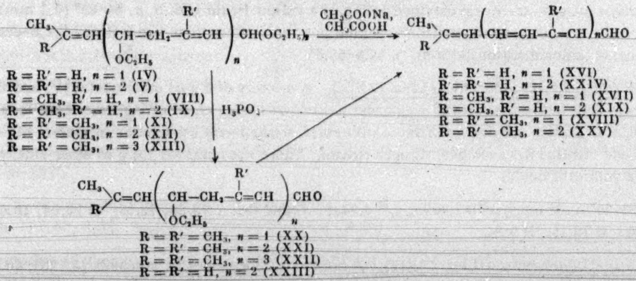
The singularity of course of the reaction in this case is evidently explained by the fact that the rate of addition of the unsaturated acetal (VII) to vinyl ethyl ether is greater than the rate of addition of the resulting saturated ether acetal (XIV).

Ether acetals, resulting from the condensation of acetals of α,β-unsaturated aldehydes with ethoxydienes, are quite stable compounds which are distillable in vacuo of 0.1 mm without decomposition and their separation does not present any difficulties. The ether acetals were converted in high yield into polyene aldehydes by heating with a mixture of sodium acetate and acetic acid (Isler method). In this manner there were prepared: 2,4,6-octatrien-8-al (XVI) from ether acetal (IV) (yield 88%); 2-methyl-2,4,6-octatrien-8-al (XVII) from ether acetal (VIII) (yield 95%); dehydrocitral (XVIII) from ether acetal(XI) (yield 89%) and 2-methyl-2,4,6,8,10-dodecapentaen-12-al (XIX) from ether acetal (IX) (yield 72%).

We found that ether acetals are quantitatively hydrolyzed to ether aldehydes under the influence of 1% orthophosphoric acid.

From ether acetals (XI), (XII), (XIII),and (V) there were obtained 4-ethoxycitral (XX), 4,8-diethoxyfarnesal (XXI), 2,6,10,14-tetramethyl-4,8,12-triethoxy-2,6,10,14-hexadecatetraen-16-al (XXII) and 4,8-diethoxy-2,6,10-dodecatrien-12-al (XXIII).

The ether aldehydes are readily converted to polyenals by the action of p-toluenesulfonic acid in toluene. By this method there were prepared 2,4,6,8,10-dodecapentaen-12-al (XXIV) and farnesal (XXV) from ether aldehydes (XXI) and (XXIII); these substances could not be prepared directly from the ether acetals (V) and (XII). 4-Ethoxycitral (XX) was converted in 92% yield into dehydrocitral (XVIII).



CH₃
R
C=CH(CH–CH₂–C=CH)ₙ CH(OC₂H₅)₂
R′
OC₂H₅
CH₃COONa,
CH₃COOH
C=CH(CH=CH–C=CH)ₙCHO
R = R′ = H, n = 1 (IV)
R = R′ = H, n = 2 (V)
R = CH₃, R′ = H, n = 1 (VIII)
R = CH₃, R′ = H, n = 2 (IX)
R = R′ = CH₃, n = 1 (XI)
R = R′ = CH₃, n = 2 (XII)
R = R′ = CH₃, n = 3 (XIII)
H₃PO₄
R = R′ = H, n = 1 (XVI)
R = R′ = H, n = 2 (XXIV)
R = CH₃, R′ = H, n = 1 (XVII)
R = CH₃, R′ = H, n = 2 (XIX)
R = R′ = CH₃, n = 1 (XVIII)
R = R′ = CH₃, n = 2 (XXV)
C=CH(CH–CH₂–C=CH)ₙ CHO
R = R′ = CH₃, n = 1 (XX)
R = R′ = CH₃, n = 2 (XXI)
R = R′ = CH₃, n = 3 (XXII)
R = R′ = H, n = 2 (XXIII)

All polyenals, except (XVII) were obtained in a crystalline form. Aldehydes (XVI), (XXIV) and (XVIII) had melting points corresponding to the literature data [5-7] and did not give a depression in mixed melting with the corresponding aldehydes isolated previously by us from the polyene condensation of crotonaldehyde and dimethylacrylaldehyde under the effect of piperidine acetate; the melting point of (XXV) corresponded to the literature data [7]. Polyenals (XIX) and (XVII) were prepared for the first time and the latter was subjected to exhaustive hydrogenation to 2-methyloctanal, the melting point of whose 2,4-dinitrophenylhydrazone agreed with the literature data [8].

Condensation of acetals of α,β-unsaturated aldehydes with ethoxyisoprene and ethoxybutadiene is a new and convenient method of synthesis of polyene aldehydes.

EXPERIMENTAL

Condensation of diethyl acetal of crotonaldehyde (III) with ethoxybutadiene (I). To a mixture of 24 g of acetal (III) and 0.12 g of boron trifluoride etherate, cooled to 0°, there was added over 1.5 hr with mechanical stirring under a nitrogen atmosphere 11 g of ethoxybutadiene (I). The mixture was stirred for 3.5 hrs at 0-10°, was then diluted with ether, washed with 5% solution of sodium hydroxide, water, dried with potassium carbonate and distilled in vacuo.

The following substances were isolated.

1) 7 g of unreacted acetal (III) with b. p. 66-70° (25 mm), $n^{22}D$ 1.4120.

2) 12 g of 4,8,8-triethoxy-2,6-octadiene (IV).

B. p. 59-61° (0.09 mm), $n^{20}D$ 1.4435, d_4^{20} 0.9026, MR 71.22; calc. 70.84. Found %: C 69.95, 69.82; H 10.74, 10.97. $C_{14}H_{26}O_3$. Calculated %: C 69.40; H 10.73.

3) 6.4 g of 4,8,12,12-tetraethoxy-2,6,10-dodecatriene (V).

B. p. 105-110° (0.05 mm), $n^{20}D$ 1.4555, d_4^{20} 0.9245, MR 100.0; calc. 99.73. Found %: C 70.90, 70.82; H 10.81, 10.63. $C_{20}H_{36}O_4$. Calculated %: C 70.60; H 10.58.

4) 3.4 g of 4,8,12,16,16-pentaethoxy-2,6,10,14-hexadecatetraene (VI).

B. p. 140-145° (0.05 mm), $n^{20}D$ 1.4610, d_4^{20} 0.9344, MR 128.8; calc. 128.62. Found %: C 71.45, 71.11; H 10.72, 10.54. $C_{26}H_{46}O_5$. Calculated %: C 71.20; H 10.57.

Condensation of 4,8,8-triethoxy-2,6-octadiene (IV) with ethoxybutadiene (I). By the above described method there was obtained from 19 g of ether acetal (IV), 3.85 g of ethoxybutadiene (I) and 0.05 g of boron trifluoride etherate, 10.5 g of unreacted ether acetal (IV), 5.1 g of ether acetal (V) and 3.1 g of ether acetal (VI).

2,4,6-Octatrien-1-al (XVI). A mixture of 3.3 g of ether acetal (IV), 1.1 g of sodium acetate, 0.7 ml of water and 11 ml of acetic acid were stirred for 4.5 hrs(95°) in a stream of nitrogen. The reaction mixture, after cooling, was poured into 30 g of ice and the resulting oil was extracted with petroleum ether. The extract was washed with 5% solution of sodium bicarbonate and water and was dried with calcined magnesium sulfate. After distillation under nitrogen there was obtained 1.45 g of a yellow liquid with b. p. 54-56° (0.1 mm) which crystallized after cooling. After two recrystallizations from petroleum ether there was isolated 2,4,6-octatrien-1-al in the form of cream colored crystals with m. p. 57.5-58.5°.

4,8-Diethoxy-2,6,10-dodecatrien-12-al (XXIII). A mixture of 5 g of ether acetal (V) and 2.5 ml of 10% orthophosphoric acid was heated with stirring under a nitrogen stream on a boiling water bath for 1.5 hr. After being cooled, the reaction mixture was diluted with ether, washed with 5% solution of sodium bicarbonate and water, dried and distilled in vacuo in a nitrogen stream. There was obtained 3.4 g of ether aldehyde (XXIII) in the form of a yellowish liquid.

B. p. 91-94° (0.03 mm), $n^{20}D$ 1.4675, d_4^{20} 0.9448. Found %: C 72.26, 72.05; H 10.04, 10.08. $C_{16}H_{26}O_3$. Calculated %: C 72.15; H 9.84.

2,4,6,8,10-Dodecapentaen-12-al (XXIV). A mixture of 3.4 g of ether aldehyde (XXIII), 60 ml of absolute toluene and 30 mg of p-toluenesulfonic acid were heated under nitrogen in a Wood metal bath at bath temperature of 125-130°. A slow distillation of toluene with alcohol took place. At the same time toluene was added to the flask to maintain a constant volume of the reaction mixture. The distillation of alcohol stopped after 1 hr (test for alcohol content in the distillate was made according to Chugaev-Tserevitinov). The reaction mixture was cooled, washed with 5% solution of sodium bicarbonate and water, dried and distilled in vacuo under a nitrogen stream. There was obtained 1.4 g of substance with b. p. 105-110° (0.1 mm) which began to crystallize during the distillation. After recrystallization from petroleum ether, then from methanol, there were isolated yellow crystals of 2,4,6,8,10-dodecapentaen-12-al (XXIV) with m. p. 158-160°.

Condensation of diethyl acetal of dimethylacrylaldehyde (VII) with ethoxybutadiene (I). To a mixture of 15 g of acetal (VII) and 0.1 g of boron trifluoride etherate, cooled to 0°, there was added with mechanical stirring in a stream of nitrogen over 30 min, 6.2 g of ethoxybutadiene (I). Then the reaction mixture was stirred for 3.5 hrs at 0-10° and was subjected to the usual treatment. After vacuum distillation there were isolated the following substances:

1) 4.8 g of original acetal (VII) with b. p. 53-63° (16 mm), $n^{18.5}D$ 1.4220.

2) 8.1 g of 2-methyl-4,8,8-triethoxy-2,6-octadiene (VIII) in the form of a colorless mobile liquid.

B. p. 80-82° (0.02 mm), $n^{20}D$ 1.4476, d_4^{20} 0.9036, MR 75.9; calc. 75.46. Found %: C 70.30, 69.99; H 10.95, 11.05. $C_{15}H_{28}O_3$. Calculated %: C 70.40; H 10.93.

3) 3.3 g of 2-methyl-4,8,12,12-tetraethoxy-2,6,10-dodecatriene (IX) in the form of a slightly yellowish liquid.

B. p. 126-130° (0.02 mm), $n^{20}D$ 1.4595, d_4^{20} 0.9264, MR 104.7; calc. 104.34. Found %: C 71.43, 71.36; H 10.74, 10.82. $C_{21}H_{38}O_4$. Calculated %: C 71.20; H 10.73.

4) 0.3 g of 2-methyl-4,8,12,16,16-pentaethoxy-2,6,10,14-hexadecatetraene (X) in the form of a yellow viscous liquid.

B. p. 155-160° (0.02 mm), $n^{20}D$ 1.4670, d_4^{20} 0.9371, MR 134.3; calc. 133.2. Found %: C 71.55, 71.68; H 10.62, 10.60. $C_{27}H_{48}O_5$. Calculated %: C 71.64; H 10.69.

Condensation of 2-methyl-4,8,8-triethoxy-2,6-octadiene (VIII) with ethoxybutadiene (II). To a mixture of 10 g of ether acetal (VIII) and 0.04 g of boron trifluoride etherate, cooled to 0°, there was added with stirring over 30 min 3.8 g of ethoxybutadiene. After 4 hrs at 0-8°, the reaction mixture was subjected to the above described treatment. After vacuum distillation at 0.06 mm, there was obtained 3.8 g of ether acetal (VIII) which had failed to react, 3.1 g of ether actal (IX) and 2.8 g of ether acetal (X). Residue, 3.3 g.

2-Methyl-2,4,6-octatrien-8-al (XVII). A mixture of 5.6 g of ether acetal (VIII), 1.8 g of sodium acetate, 1.1 ml of water and 17.5 ml of acetic acid was heated in nitrogen stream at 95° with mechanical stirring for 4.5 hrs. After the usual treatment, the product was vacuum distilled in a stream of nitrogen. There was obtained 2.8 g of 2-methyl-2,4,6-octatrien-8-al (XVII) with b. p. 63-64° (0.02 mm). Aldehyde (XVII) was an uncrystallizing yellow liquid with the odor of 2,4,6-octatrien-8-al (XVI). The 2,4- dinitrophenylhydrazone of aldehyde (XVII) melted at 204-205° (from a mixture of chloroform and methanol).

λ_{max} in isooctane 321, 396.5 mμ. Found %: N 17.81, 17.76. $C_{15}H_{16}O_4N_4$. Calculated %: N 17.73.

2-Methyl-2,4,6,8,10-dodecapentaen-12-al (XIX). A mixture of ether acetal (IX; 3.4 g), 1.6 g of sodium acetate, 1 ml of water and 16 ml of acetic acid was heated at 95° in nitrogen stream for 5 hrs with mechanical stirring. After the usual treatment and vacuum distillation there was obtained 1.4 g of 2-methyl-2,4,6,8,10-dodecapentaen-12-al (XIX) with b. p. 100-105° (0.06 mm), which crystallized soon to a yellow crystalline mass. After two recrystallizations from ethyl alcohol, the aldehyde (XIX) was isolated in the form of golden yellow leaflets with m. p. 136-137°.

λ_{max} (in ethanol)234.5 mμ (log ε 3.96), 271.5 mμ (log ε 3.97), 391 mμ (log ε 4.67). Found %: C 83.50, 83.33; H 8.68, 8.33. $C_{13}H_{16}O$. Calculated %: C 83.00; H 8.52.

Condensation of diethyl acetal of dimethylacrylaldehyde (VII) with ethoxyisoprene (II). To a mixture of 204 g of acetal (VII) and 13 ml of 10% solution of zinc chloride in ethyl acetate there was added over 2.5 hrs at 20° with stirring 35.6 g of ethoxyisoprene; the temperature rose thereupon to 27°. Then the reaction mixture was stirred for 1.5 hr at room temperature and 45 min at 35-40°, after which it was diluted with ether, washed with 5% solution of sodium hydroxide and water, dried with potassium carbonate and vacuum distilled. The following products were isolated:

1) 159 g of the initial acetal (VII) with b. p. 65-68° (24 mm), $n^{18}D$ 1.4215.

2) 38.0 g of 2,6-dimethyl-4,8,8-triethoxy-2,6-octadiene (XI) in the form of a colorless liquid.

B. p. 80-81° (0.1 mm), $n^{20}D$ 1.4517, d_4^{20} 0.9120, MR 79.82; calc. 80.08. Found %: C 71.28, 71.20; H 11.10, 11.11. $C_{16}H_{30}O_3$. Calculated %: C 71.08; H 11.19.

3) 18.0 g of 2,6,10-trimethyl-4,8,12,12-tetraethoxy-2,6,10-dodecatriene (XII).

B. p. 124-126° (0.04 mm), $n^{20}D$ 1.4618, d_4^{20} 0.9200, MR 114.3; calc. 113.59. Found %: C 72.24, 72.26; H 10.91, 10.91. $C_{23}H_{42}O_4$. Calculated %: C 72.18; H 11.06.

4) 7.8 g of 2,6,10,14-tetramethyl-4,8,12,16,16-pentaethoxy-2,6,10,14-hexadecatetraene (XIII) in the form of a yellowish viscous liquid.

B. p. 164-168° (0.07 mm), $n^{20}D$ 1.4710, d_4^{20} 0.9298. Found %: C 73.00, 72.84; H 11.04, 10.84. $C_{30}H_{54}O_5$. Calculated %: C 72.85; H 11.00.

Condensation of 2,6-dimethyl-4,8,8-triethoxy-2,6-octadiene (XI) with ethoxyisoprene (II). By the above described method there was prepared from 12 g of ether acetal (XI), 2.5 g of ethoxyisoprene and 0.6 ml of 10% solution of zinc chloride in ethyl acetate, 7.8 g of the initial ether acetal (XI), 3.45 g of ether acetal (XII) and 1.4 g of ether acetal (XIII).

4-Ethoxycitral (XX). A mixture of 8.1 g of ether acetal (XI), 1 g of 1% orthophosphoric acid and 2.5 ml of ethyl alcohol was stirred in a stream of nitrogen for 1.5 hrs at room temperature. The reaction mixture became homogeneous after 15 min. The mixture was diluted with ether, washed with 5% solution of sodium bicarbonate and water, dried with magnesium sulfate and distilled in vacuum in nitrogen atmosphere. There was obtained 5.3 g of 4-ethoxycitral (XX) in the form of colorless (yellowing on standing) liquid which did not smell of lemon peel.

B. p. 58-60° (0.06 mm), $n^{20}D$ 1.4762, d_4^{20} 0.9247, MR 59.89; calc. 58.34. λ_{max} (in ethanol) 240 mμ (log ε 4.132), 326 mμ (log ε 1.956). Found %: C 73.29, 73.46; H 10.10, 9.98. $C_{12}H_{20}O_2$. Calculated %: C 73.41; H 10.27.

Dehydrocitral (XVIII). a) A mixture of 3.2 g of 4-ethoxycitral (XX), 50 ml of absolute toluene and 5 mg of p-toluenesulfonic acid was heated in a nitrogen stream on a Wood metal bath at bath temperature of 110-130°. A slow distillation of toluene and alcohol took place; after 20 min the distillation of alcohol ceased (test for alcohol content in the distillate made with Chugaev-Tserevitinov method). The reaction mixture was cooled and washed with 5% solution of sodium bicarbonate and water, dried with magnesium sulfate and distilled in vacuo in nitrogen atmosphere. There was obtained 2.25 g of dehydrocitral (XVIII) with b. p. 57-60° (0.05 mm) which crystallized on cooling. After two recrystallizations from petroleum ether there were isolated the light yellow crystals of (XVIII) with m. p. 39-40°.

b) A mixture of 10 g of ether acetal (XI), 3.2 g of sodium acetate, 2 ml of water and 30 ml of acetic acid was heated to 95° in nitrogen stream with stirring for 5 hrs. After the usual treatment and distillation, there was obtained 4.8 g of dehydrocitral (XVIII) with b. p. 64-65° (0.06 mm), m. p. 39-40° (from petroleum ether).

2,6,10-Trimethyl-4,8-diethoxy-2,6,10-dodecatrien-12-al (4,8-diethoxyfarnesal) (XXI). A mixture of 6.5 g of ether acetal (XII), 0.75 g of 1% orthophosphoric acid and 1.75 ml of ethyl alcohol was shaken in a closed flask at room temperature. The layers disappeared after 10 min; after further 1.5 hrs the mixture was subjected to the usual treatment and vacuum distillation in nitrogen atmosphere. There was obtained 5.02 g of 4,8-diethoxyfarnesal (XXI) in the form of a yellowish liquid.

B. p. 114-115° (0.04 mm), $n^{20}D$ 1.4875, d_4^{20} 0.9419, MR 94.28; calc. 91.84. Found %: C 73.99, 74.13; H 10.43, 10.44. $C_{19}H_{32}O_3$. Calculated %: C 73.98; H 10.46.

Farnesal (XXV). A mixture of 2 g of undistilled 4,8-diethoxyfarnesal (XXI), 50 ml of absolute toluene and 6 mg of p-toluenesulfonic acid was heated in nitrogen atmosphere in a Wood metal bath at bath temperature of 120-125°. A slow distillation of toluene and alcohol took place and simultaneously with this distillation toluene was gradually added to the flask so as to maintain a constant volume of the mixture. After 1 hr the distillation of alcohol ceased (test for alcohol content in the distillate was made according to Chugaev-Tserevitinov). After the usual treatment and vacuum distillation in nitrogen atmosphere there was obtained 0.85 g of substance with b. p. 115-120° (0.05 mm), which began to crystallize during the distillation. After two recrystallizations there was isolated farnesal (XXV) in the form of yellow leaflets with m. p. 119-120° (from ethyl alcohol).

λ_{max} (in ethanol), 239 mμ (log ε 3.92), 279 mμ (log ε 3.97), 386 mμ (log ε 3.99). Found %: C 83.40; H 9.41. $C_{15}H_{20}O$. Calculated %: C 83.23; H 9.32.

2,6,10,14-Tetramethyl-4,8,12-triethoxy-2,6,10,14-hexadecatetraen-16-al (XXIII). A mixture of 3 g of ether acetal (XIII), 0.75 g of 1% orthophosphoric acid and 1.75 ml of ethyl alcohol was shaken in a closed flask at room temperature. After 1.5 hr the mixture was subjected to the usual treatment. There was obtained 1.9 g of ether aldehyde (XXIII) in the form of a viscous yellow liquid.

B. p. 158-162° (0.1 mm), $n^{20}D$ 1.4954, d_4^{20} 0.9452. Found %: C 74.06, 74.30; H 10.24, 10.20. $C_{26}H_{54}O_6$. Calculated %: C 74.27; H 10.54.

Condensation of diethyl acetal of dimethylacrylaldehyde (VII) with vinyl ethyl ether. To a mixture of 6.4 g of acetal (VII) and 1 ml of 10% solution of zinc chloride in ethyl acetate, heated to 55-60°, there was added over 30 min with stirring 3.2 g of vinyl ethyl ether. The mixture was heated for 4 hrs at 60° and was then distilled in vacuo. There was obtained 6.6 g of 2-methyl-4,6,6-triethoxy-2-hexene (XIV).

B. p. 63-65° (0.01 mm), $n^{20}D$ 1.4295, d_4^{20} 0.8906, MR 66.73; calc. 66.70. Found %: C 68.08, 67.90; H 11.15, 11.23. $C_{13}H_{26}O_3$. Calculated %: C 67.85; H 11.3.

2-Methyl-2,4-hexadien-6-al (XV). A mixture of 10.4 g of ether acetal (XIV), 3.7 g of sodium acetate, 2.5 ml of water and 36 ml of acetic acid was heated at 95° in nitrogen atmosphere with stirring for 4 hrs. After the usual treatment and vacuum distillation there was obtained 4.4 g of 2-methyl-2,4-hexadien-6-al (XV).

B. p. 90-91° (23 mm), $n^{20}D$ 1.5541, d_4^{20} 0.9036. λ_{max} (in methanol) 285 mμ (log ε 4.46). Found %: C 76.34, 76.18; H 9.26, 9.22. $C_7H_{10}O$. Calculated %: C 76.3; H 9.09.

The 2,4-dinitrophenylhydrazone of the aldehyde (XV) has m. p. 200-202° (from a mixture of methyl alcohol and ethyl acetate).

λ_{max} (in heptane) 266.5, 303, 379.5 mμ. Found %: N 19.31, 19.45. $C_{13}H_{14}O_4N_4$. Calculated %: N 19.32.

SUMMARY

Condensation of acetals with ethoxyisoprene and ethoxybutadiene was realized for the first time.

The use of ethoxyisoprene permits one to lengthen a carbon chain by 5 carbon atoms with introduction of 2 double bonds and an aldehyde group conjugated to them (in case of addition of one molecule of ethoxyisoprene) as well as by 10 carbon atoms with introduction of 4 double bonds (in case of addition of 2 molecules of ethoxyisoprene), which represents the new and simple method of synthesis of polyene aldehydes of the isoprenoid type.

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SYNTHESIS OF DIENIC ACIDS FROM α-PYRONES

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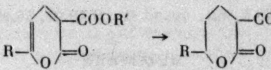
Recently we described a simple and convenient method of synthesis of esters of α-pyrone-3-carboxylic acids [1] from β-chlorovinyl ketones. The present paper describes the experiments directed toward the utilization of the indicated α-pyrone-3-carboxylic acid for the preparation of difficultly accessible aliphatic acids and their derivatives.

With this as a goal we first examined the hydrogenation of derivatives of α-pyrone. We succeeded in showing that α-pyrone-3-carboxylic acids and their esters are smoothly hydrogenated over palladium on barium sulfate and are transformed into the corresponding α-carboxy (or α-carbethoxy)-δ-lactones (yield: 70-85%).

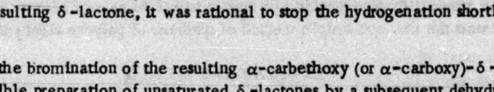


(I) $R = CH_3$, $R' = H$; (II) $R = CH_3$, $R' = C_2H_5$; (III) $R = C_5H_{11}$, $R' = C_2H_5$.

It should be noted that the hydrogenation proceeds rather slowly, which is not unexpected since it is well known that α-pyrones show some of the symptoms of aromaticity. In order to avoid the processes connected with hydrogenolysis of the resulting δ-lactone, it was rational to stop the hydrogenation shortly before the uptake of 2 moles of hydrogen.

Then we studied the bromination of the resulting α-carbethoxy (or α-carboxy)-δ-lactones for solution of the problem of the possible preparation of unsaturated δ-lactones by a subsequent dehydrobromination. Since the compounds (I)-(III), prepared by us, are cyclic analogs of malonic acid and its derivatives, the bromination was accomplished under mild conditions. The bromination of the lactone of α-carboxy-δ-hydroxycaproic acid (I) was accompanied by decarboxylation, which complicated the reaction. Bromination of the appropriate esters, specifically lactones of α-carbethoxy-δ-hydroxycaproic (II) and -decanoic (III) acids can be accomplished by the action of bromine in the presence of pyridine. However, the isolation of the resulting bromides is connected with great difficulties since they partly lose the elements of hydrogen bromide during distillation and for this reason cannot be isolated in an analytically pure state. Owing to this, it is rational to run the dehydrobromination without isolating the bromides in a pure state.

At first we attempted to accomplish the transformation of the thus obtained α-bromo-α-carbethoxy-δ-lactones into the corresponding α,β-unsaturated δ-lactones, to which belongs a series of physiologically active substances parasorbic acid, massoya lactone). However, all attempts to dehydrobrominate the above bromides were accompanied by more complex changes connected with the opening of the lactone ring. More interesting was the result obtained on treatment of the indicated bromides with diethylaniline with heating. As the result of this reaction there were isolated esters of the corresponding α,β,γ,δ-doubly unsaturated aliphatic acids – sorbic and 2,4-decadienoic acids.



$$\rightarrow R{-}CH{=}CH{-}CH{=}CH{-}COOC_2H_5,\qquad R = CH_3,\ C_5H_{11}$$

The mechanism of this interesting transformation was not clarified by us, but it is easy to think that in it there first takes place a dehydrobromination, followed by ring opening and decarboxylation. Transformations of a similar type, which proceed at high temperatures, are known in the series of β-lactones [2], and our compounds are vinylogs of such substances. The presence of a tertiary amine in this case must aid ring opening. An attempt to realize the loss of hydrogen bromide by the action of aqueous and alcoholic solutions of potassium hydroxide failed to give the desired results. A study of the reaction products formed thereby showed that in this case there takes place a replacement of bromine by hydroxy and methoxy groups instead of the cleavage of hydrogen bromide.

The path of preparation of difficultly accessible dienic acids with a conjugated bond system, discovered by us, has an undoubted preparative interest when one considers the accessibility of the initial 3-carbethoxy-α-pyrones and the good yields. Esters of dienic acids were hydrolyzed by us to the corresponding acids. The thus obtained sorbic and 2,4-decadienoic acid corresponded to the trans-trans isomers by their constants. It is impossible to say whether or not the esters prepared during the treatment with diethylaniline were also trans-trans isomers, since their hydrolysis can be accompanied by isomerization [3].

In conclusion it should be noted that the dienoic acids prepared by us can be readily converted into the corresponding α,β-unsaturated δ-lactones [4], which can thus be prepared from the corresponding α-pyrones by a somewhat more complex route than proposed by us at first.

EXPERIMENTAL

Lactone of α-carboxy-δ-hydroxycaproic acid. A suspension of 10.0 g (0.065 mole) of 6-methyl-α-pyrone-3-carboxylic acid in 50 ml of ether was hydrogenated in the presence of 0.5 g of palladium on barium sulfate (palladium content 5%) until the uptake of 2.85 liters of hydrogen (0°, 760 mm). The catalyst was filtered off, ether was evaporated and the remaining oil crystallized partially after many days of drying in a vacuum desiccator. The crystals were pressed on a porous plate and recrystallized from a mixture of benzene and petroleum ether; yield, 7.15 g (69.6%); m. p. 75-76° (decomp.).

Found %: C 53.65, 53.61; H 6.62, 6.61. $C_7H_{10}O_4$. Calculated %: C 53.16; H 6.37.

The lactone of α-carboxy-δ-hydroxycaproic acid forms colorless crystals, soluble in water, alcohol, ether and benzene.

Lactone of α-carbethoxy-δ-hydroxycaproic acid. 6-Methyl-3-carbethoxy-α-pyrone (23.1 g, 0.13 mole) was hydrogenated in 100 ml of alcohol over 2 g of palladium on barium sulfate (palladium content 5%) until the uptake of 4.9 liters (0.22 mole) of hydrogen (0°, 760 mm), after which the catalyst was filtered off, the alcohol distilled off and the residue was vacuum distilled collecting the fraction with b. p. 134-136° (4 mm); yield: 18.9 g (78%). After two distillations the substance had the following constants:

B. p. 119-120° (1 mm), d_4^{20} 1.1311, $n^{20}D$ 1.4550, MR_D 44.66; calc. 44.87. Found %: C 58.26, 58.25; H 7.68, 7.68. $C_9H_{14}O_4$. Calculated %: C 53.05; H 7.58.

The lactone of α-carbethoxy-δ-hydroxycaproic acid is a colorless oil, soluble in the majority of organic solvents.

Lactone of α-carbethoxy-δ-hydroxycapric acid. 6-Amyl-3-carbethoxy-α-pyrone (38.5 g; 0.16 mole) was hydrogenated over 2.2 g of palladium on barium sulfate (palladium content 5%) in 50 ml of alcohol until the uptake of 6.9 liters of hydrogen (0.31 mole) (0°, 760 mm). The catalyst was then filtered off, the alcohol was distilled and the residue vacuum distilled, collecting the fraction with b. p. 170-172° (6 mm); yield: 32.5 (84%). After two redistillations the substance had the following constants:

B. p. 170-172° (6 mm), d_4^{20} 1.0429, $n^{20}D$ 1.4561, MR_D 63.09; calc. 63.34. Found %: C 64.09, 64.10; H 9.14, 9.32. $C_{13}H_{22}O_4$. Calculated %: C 64.43; H 9.15.

The lactone of α-carbethoxy-δ-hydroxycapric acid was an oily liquid with a characteristic odor, soluble in the usual organic solvents.

Sorbic acid. To a solution of 1.68 g (0.09 mole) of the lactone of α-carbethoxy-δ-hydroxycaproic acid in 30 ml of anhydrous carbon tetrachloride there was added slowly with cooling and stirring 15.8 g (0.08 mole) of N-bromosuccinimide, after which the mixture was heated for 2 hrs at 55°. On the following day the precipitated succinimide was filtered off, the filtrate was evaporated and the residue distilled in vacuum, collecting the fraction which boiled with strong decomposition at 149-152° (3 mm); yield, 4.7 g. In all the following redistillations, a strong decomposition was observed with formation of insignificant amounts of a lower boiling fraction. A mixture of 12 g of the resulting bromide and 23 g of freshly distilled diethylaniline was heated on an oil bath for 1 hr at the bath temperature of 130-140°; after cooling, the mixture was diluted with absolute ether, the diethylaniline hydrobromide was filtered off, washed with absolute ether, the ethereal solution washed with 10% solution of hydrochloric acid for the removal of diethylaniline (4 times with 100 ml), dried over magnesium sulfate and vacuum distilled for the isolation of the ethyl ester of sorbic acid; yield, 4.5 g (37%); b. p. 74-76° (14 mm). The ether ester of sorbic acid (3.7 g, 0.026 mole) was boiled for 30 min with 20 ml of 20% aqueous solution of sodium hydroxide, then was treated with enough water to dissolve the sodium sorbate which had precipitated during the saponification, extracted twice with ether and the aqueous layer, after the separation of ether, was sucked with a stream of air pulled with a water pump for 20 min to remove traces of residual ether, acidified, the precipitated sorbic acid being filtered off, and dried in vacuo over phosphoric anhydride; yield 1.9 g (64.4%); m. p. 132-133° (from water).

Found %: C 64.14, 64.15; H 7.30, 7.28. $C_6H_8O_2$. Calculated %: C 64.27; H 7.19.

Literature data [3]: trans-trans-sorbic acid, m. p. 134.5°.

Ethyl ester of 2,4-decadienoic acid. To a solution of 15.5 g (0.07 mole) of α-carbethoxy-δ-hydroxycapric acid in 30 ml of anhydrous carbon tetrachloride there was added 6 ml of dry pyridine, after which there was slowly added, with cooling and stirring, a solution of 3.8 ml of bromine in 25 ml of carbon tetrachloride. After completion of bromine addition, the pyridine hydrobromide was filtered off, the mother liquor was evaporated in vacuo from a water pump and to the residue there was added 22 ml of diethylaniline; the mixture was heated for 1 hr on an oil bath at 135-140°; on cooling, the reaction mixture was diluted with absolute ether, the precipitated diethylaniline hydrobromide was filtered off and washed with absolute ether, the ether was distilled from the filtrate and the residue was vacuum distilled, collecting the fraction with b. p. 106-115° (5 mm). The crude product containing some diethylaniline was dissolved in 50 ml of ether, washed with 10% hydrochloric acid (3 times 25 ml), twice with water, the ethereal layer removed and dried over magnesium sulfate and freed of ether by distillation; the residual ethyl ester of 2,4-decadienoic acid was vacuum distilled, collecting the fraction with b. p. 108-110° (5 mm); yield, 3.5 g (28%). After two distillations, the product had the following constants:

B. p. 109-110° (5 mm), d_4^{20} 0.9155, $n^{20}D$ 1.4720. Found %: C 73.29, 73.40; H 10.53, 10.45. $C_{12}H_{20}O_2$. Calculated %: C 73.43; H 10.27.

2,4-Decadienoic acid. Ethyl ester of 2,4-decadienoic acid (2.1 g; 0.011 mole) was boiled for 30 min with 10 ml of 20% aqueous solution of potassium hydroxide and 5 ml of methanol. After cooling, there was added 20 ml of water, extracted twice with ether, the aqueous layer was acidified and extracted with ether (3 times 20 ml), the ethereal extracts were dried with magnesium sulfate, freed of ether by distillation and the residue was vacuum distilled, collecting the fraction with b. p. 144-147° (3 mm); yield, 1.3 g (73%). After two distillations the substance had the following constants:

B. p. 144-145° (2 mm), $n^{20}D$ 1.4938. Found %: C 71.24, 71.13; H 9.70, 9.45. $C_{10}H_{16}O_2$. Calculated %: C 71.39; H 9.59.

The benzylthiuronium salt was prepared as usual; m. p. 167°.

Found %: N 8.07, 8.10. $C_{18}H_{26}O_2N_2S$. Calculated %: N 8.38.

Literature data [5]: for trans-trans-2,4-decadienoic acid: $n^{20}D$ 1.4918; benzylthiuronium salt, m. p. 175°.

SUMMARY

1. It was shown that α-carbethoxy-δ-lactones are formed in high yield during the hydrogenation of 6-alkyl-3-carbethoxy-α-pyrones.

2. A new method of preparation of aliphatic dienic acids was developed by the way of bromination of corresponding α-carbethoxy-δ-lactones with a subsequent treatment of the bromides with diethylaniline.

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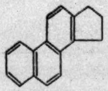
DIPHENSUCCINDANE AND 2,6-DIHYDROXYDIPHENSUCCINDANE

S. F. Torf and N. V. Khromov-Borisov

Steroidal hormones are derivatives of cyclopentanophenanthrene (I). Diphensuccindane (indano-2',1':1,2-indane) (II) has some elements of structural similarity to (I).* Therefore, the synthesis and the study of the corresponding derivatives has points of interest in the search for new synthetic medicinal substances, as well as in the study of the link between the chemical structure and the pharmacological action in this series of compounds.



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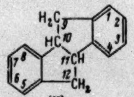

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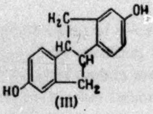
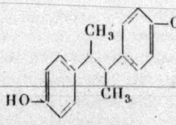


(III)

We synthesized several derivatives of diphensuccindane, among which we describe in this paper the synthesis of diphensuccindane itself and of its 2,6-dihydroxy derivative (III).

It is known that p,p'-dihydroxy derivatives of diphenylethane hydrocarbons, containing alkyl radicals at the ethane carbon atoms, possess some estrogenic properties. The most active in this respect are p,p-dihydroxymeso-2,3-diphenylbutane (IV) [1] and p,p-dihydroxy-meso-3,4-diphenylhexane (synestrol) (V) [1]. The high estrogenic activity of the latter is explained in part by its structural similarity to estradiol (VI) [1]— natural hormone, having high estrogenic activity.



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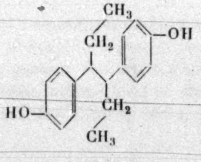

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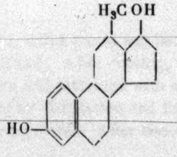

(VI)

2,6-Dihydroxydiphensuccindane (III) is a closed analog of p,p'-dihydroxy-2,3-diphenylbutane (IV) and in its tetracyclic structure possesses a greater degree of similarity to estradiol than does p,p'-dihydroxy-2,3-diphenylbutane.

Over 20 papers have been published in the literature, relative to the derivatives of diphensuccindane, mainly substituted in positions 9, 10, 11 or 12. Among the derivatives substituted in the benzene rings, there have been described 2,6-dinitrodiphensuccindanedione (VII) [2] and 2,6-diaminodiphensuccindanedione (VIII) [2] (see diagram at top of following page).

The 2- and 6-positions of nitro groups in 2,6-dinitrodiphensuccindanedione were assigned on the basis of the following data. By oxidation of this dinitro product [2] there was obtained in 57% yield 4-nitrophthalic acid;

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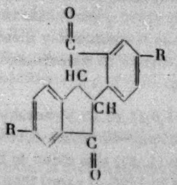
* In the present paper we do not consider the stereoisomerism of these compounds.



(VII) $R = NO_2$
(VIII) $R = NH_2$
(IX) $R = H$

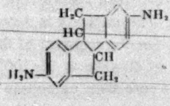
the same acid may be obtained in the oxidation of 3,7-dinitrodiphensuccindanedione. However, the 3- and 7-positions of the nitro groups are excluded by the authors [2] on the basis of the meta-orienting effect of keto groups in the nitration of the diphensuccindanedione (IX).

The first derivative of diphensuccindane series – diphensuccindanedione (IX) was prepared by Reimer [3]. The structure of this derivative was later established by Roser [4] without a clarification of the spatial configuration.

We prepared diphensuccindanedione by Reimer's method [3], by heating meso-diphenylsuccinic acid [5] with sulfuric acid, but at lower temperature [6]. Diphensuccindanedione was also prepared by us from the racemate of diphenylsuccinic acid [5] but, as already noted in the literature [4], the yield of diphensuccindanedione in this case was considerably lower.

The synthesis of 2,6-dihydroxydiphensuccindanedione, starting with diphensuccindanedione was conducted as follows: diphensuccindanedione was converted by the previously described method [2] into 2,6-dinitrodiphensuccindanedione and further into 2,6-diaminodiphensuccindanedione [2]. The experiments run by us with the reduction of 2,6-diaminodiphensuccindanedione by the Clemmensen method for the preparation of 2,6-diaminodiphensuccindane (X) failed to give positive results. Therefore (VIII) was at first acetylated, then reduced by Clemmensen method to 2,6-diacetamidodiphensuccindane (XI), from which the 2,6-diaminodiphensuccindane was obtained after hydrolysis. 2,6-Dihydroxydiphensuccindane was prepared from the latter compound by diazotization reaction and further decomposition of the diazo compound.

It should be noted that during boiling of the diamino product (VIII) with excess acetic anhydride until the precipitate dissolved, there was formed a tetraacetyl derivative. This was isolated and analyzed by us, but its structure was not studied in more detail. This compound may have the structure of 2,6-bis-(diacetylamino) diphensuccindanedione (XII) or 2,6-diacetylamino-9, 12-diacetoxydiphensuccindanedione (XIII). Two acetyl are cleaved on boiling this compound with aqueous acetic acid.



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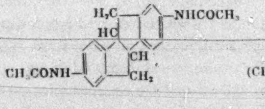
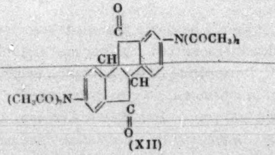
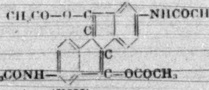


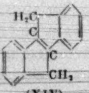
(XI)



(XII)



(XIII)

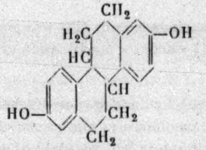


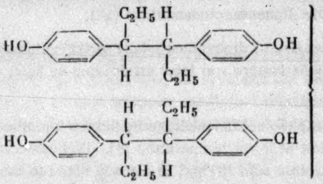
(XIV)

For a further study of the properties of diphensuccindane (II) we developed a convenient method of its preparation from diphensuccindanedione (IX). In the literature there is described a synthesis of diphensuccindane by the way of reaction of diphensuccindanedione with phosphorus and hydroiodic acid [4], as well as by catalytic reduction of diphensuccindene (XIV) [7], prepared in two steps from diphensuccindanedione [7]. We prepared diphensuccindane by reduction of diphensuccindanedione by Clemmensen method in sulfuric acid medium with simultaneous distillation of the reaction products with steam.

Tests of estrogenic properties of 2,6-dihydroxydiphensuccindane, made by A. I. Podlesnaia, showed that this compound has insignificant estrogenic activity (1000 γ per mouse in 54% of cases). Thus, in the strength of its estrogenic action 2,6-dihydroxydiphensuccindane is considerably closer to the racemate of p,p'-dihydroxy-2,3-diphenylbutane (1000 γ per rat in 100% of cases) than to its stereoisomer p,p'-dihydroxy-meso-2,3-diphenylbutane (0.5 γ [1], 10 γ [1] per rat in 100% of cases).

It is interesting to note that 2,8-dihydroxy-5,6,11,12,13,14-hexahydrochrysene (XV) described in the literature [8], which in its structure is a closed analog of p,p'-dihydroxy-3,4-diphenylhexane is in the strength of its estrogenic action (1000 γ per rat in 100% of cases [1, 8]) also closer to the racemate of p,p'-dihydroxy-3,4-diphenylhexane (XVI) (500 γ [1], 1000 γ [1] per rat in 100% of cases) than to p,p'-dihydroxy-meso-3,4-diphenylhexane (synestrol) (V) (0.2 γ per rat in 100% of cases [1]).


(XV)


(XVI)

EXPERIMENTAL

Diphensuccindanedione. To 320 ml of concentrated sulfuric acid there was added 75 g of meso-diphenylsuccinic acid, after which the mixture was stirred and heated for 20-30 min at 110°. The resulting brown solution was stirred at 110° for 10 min longer, then poured in a stream into a 2-liter beaker half-filled with ice. After several hours, the precipitate was filtered off and washed with water. The weight of the precipitate, dried at 50°, was 29 g. After recrystallization from 1400 ml of alcohol there was obtained 22 g of diphensuccindanedione with m. p. 204-206°, the product being colorless. From the mother liquor, after the distillation of the main bulk of alcohol, there was isolated an additional 3 g of the substance with yellow color and m. p. 203-205°. Yield 38.5%.

In some experiments the product precipitated in the form of very fine and difficulty filterable solid. For facilitation of filtration, the precipitate along with the liquid, was heated for 40 min on a boiling water bath, as the result of which the precipitate was coarsened and was filtered without difficulty. The yield in these cases reached 50%.

It should be noted that diphensuccindanedione (m. p. 204-206°), recrystallized from alcohol, contains insignificant amounts of a higher melting impurity which has acid properties. The impurity is detected by observation of the melting of the substance under a microscope on a hot stage [9]. For the removal of this impurity from the main substance, 50 g of diphensuccindanedione was dissolved in 300 ml of dioxane at 95-100° and the hot solution was poured in a thin stream into 450 ml of 1.5% aqueous solution of potassium carbonate with energetic stirring. A precipitate of diphensuccindanedione forms thereby while the liquid shows an alkaline reaction to phenolphthalein. After stirring for 40 min, the mixture was set aside for several hours after which the precipitate was filtered off, washed with water and dried at 100°. The thus purified diphensuccindanedione (48.6 g) melted in a capillary at 203-205° (uncorrected), while on a hot stage it melted at 208-209°, and it melted homogeneously. For preparation of diphensuccindanedione from the racemate of diphenylsuccinic acid, purified through the barium salt and recrystallized from water, the yield reaches but 8.7%. The mixed melting point with diphensuccindanedione prepared from meso-diphenylsuccinic acid gave no depression.

2,6-Dinitrodiphensuccindanedione. 20 g of diphensuccindanedione was added over 40 min to a solution of 40 g of potassium nitrate in 216 ml of concentrated sulfuric acid at 3-8°. After this the stirring was continued for 3 hrs without cooling, whereupon the temperature of the solution rose to 18°. The solution was poured on ice, the resulting precipitate was filtered off, washed with water and dried at 50°. Weight, 27.6 g. The precipitate was boiled for one hour with dilute acetic acid (75 ml of acetic acid and 75 ml of water), and the undissolved portion was filtered off while hot, boiled with 200 ml of acetic acid for one hour, the mixture was then treated with 30 ml of water, the mixture boiled for 30 min longer, the undissolved precipitate filtered off while hot, washed with hot dilute acetic acid and dried at 100°. The weight of 2,6-dinitrodiphensuccindanedione was 10.9 g (35.7%), m. p. 239-241°, yellowing at 236°. The precipitate was recrystallized from 300 ml of ethylene chloride. After cooling of the filtrate in a freezing mixture there was obtained 9.6 g of product which was colorless and had a flesh shade; m. p. 239-241°. Additional 1 g of product with m. p. 239-241° was isolated after distillation of the bulk of the solvent.

Found %: N 8.43, 8.34. $C_{16}H_8O_6N_2$. Calculated %: N 8.64.

2,6-Diaminodiphensuccindanedione. A mixture of 10 g of 2,6-dinitrodiphensuccindanedione, 22.5 g of granulated tin and 132 ml of concentrated hydrochloric acid was heated for 6 hrs on a boiling water bath. Then the mixture was refluxed for 20-40 min until the small residual precipitate had dissolved. The mixture of liquid and precipitate, obtained after cooling, was saturated with hydrogen chloride, with water cooling. On the following day, the precipitate was filtered off on a porous glass filter, washed with concentrated hydrochloric acid, dissolved in dilute hydrochloric acid (300 ml of water and 12 ml of concentrated hydrochloric acid), the tin was precipitated from it with hydrogen sulfide and the filtrate was evaporated to dryness.

The residue was dissolved in dilute hydrochloric acid (150 ml of water and 4 ml of concentrated hydrochloric acid) and the filtered solution was poured into excess dilute ammonium hydroxide. A very fine, difficultly filterable precipitate formed. After standing for 4 hrs, the precipitate was filtered off, washed with water and dried at 100°. The weight of 2,6-diaminodiphensuccindanedione was 6.2 g (76%); light yellow (lemon) colored solid, which did not melt at 325°.

Found %: N 10.50, 10.60. $C_{16}H_{12}O_2N_2$. Calculated %: N 10.60.

Tetraacetyl derivative (XII) or (XIII). A mixture of 1 g of 2,6-diaminodiphensuccindanedione and 65 ml of acetic anhydride was refluxed for 4-5 hrs until the precipitate had dissolved. The precipitate did not reform on cooling the solution. From the yellow solution, the acetic anhydride was distilled in vacuo from a boiling water bath. The dry residue was dissolved at room temperature in 20 ml of chloroform, the chloroform solution was filtered from a precipitate (0.15 g), which did not melt at 300°, and the filtrate was gradually diluted with 80 ml of petroleum ether. The resulting precipitate was filtered off. The weight of the air-dried residue was 1.5 g. This precipitate was refluxed with 30 ml of dry benzene, the solution was filtered from a slight precipitate (0.07 g) while warm and the slightly warm solution was diluted with an equal volume of petroleum ether. The resulting precipitate was filtered off. The weight of air-dry tetraacetyl derivative was 1.15 g (70.1%); it changes at 210°, m. p. 218-220°. It has a flesh color.

Found %: C 66.42, 66.24; H 4.88, 4.77; N 6.38, 6.79. $C_{24}H_{20}O_6N_2$. Calculated %: C 66.67; H 4.66; N 6.48.

2,6-Diacetylaminodiphensuccindane (XI). A mixture of 5.2 g of 2,6-diaminodiphensuccindanedione and 300 ml of acetic anhydride was refluxed for 5 hrs until the precipitate had dissolved. On the following day 25 g of zinc dust was stirred for 15 min with a solution of 7 ml of acetic acid and 120 ml of water, the solution was decanted, the remaining zinc was stirred for 15 min with 25 ml of 5% solution of mercuric chloride, after which the metal was filtered off, washed several times with water and the wet precipitate of amalgamated zinc was added to the above-described solution of the tetraacetyl derivative in acetic anhydride. The solution was heated to boiling and to the boiling solution there was added 150 ml of water over 2 hrs. The addition of water through the reflux condenser was done at first in very small portions – 1-3 ml each, since after each such addition the mixture boiled up energetically. After completion of addition of water, the mixture was refluxed for 4 hrs longer. On the following day the precipitate which had formed overnight was dissolved by heating. The solution was refluxed for 5 hrs longer, while 150 ml of water was being added during the first 2 hrs. The hot mixture was filtered from the zinc residue (3.3 g). The resulting precipitate after cooling of the mixture was separated and washed with dilute acetic acid, then was stirred with water, filtered and dried. Its weight was 3.2 g. The precipitate was recrystallized from 50 ml of acetic acid. There was obtained 3.1 g (49.2%) of 2,6-diacetylaminodiphensuccindane, dried at 110°; it was white with a grey shade. M. p. 238-241°.

Found %: N 8.42, 8.55. $C_{20}H_{20}O_2N_2$. Calculated %: N 8.74.

2,6-Diaminodiphensuccindane (X). A mixture of 3 g of 2,6-diacetylaminodiphensuccindane, 300 ml of water and 20 ml of concentrated hydrochloric acid was refluxed with stirring in a flask of 1500 ml capacity (the mixture foams) for about 15 hrs until the precipitate had dissolved; the heating was done with interruptions while stirring was employed only during the first half of heating since the bumping of the precipitate ceased gradually. Then the solution was refluxed with 1 g of activated carbon and the hot filtrate was poured into dilute solution of alkali. The precipitate was filtered off after cooling. The weight of the precipitate, dried at 60°, was 1.55 g. The precipitate was dissolved with heating in 30 ml of alcohol (a small amount of impurity failed to dissolve), after which 80 ml of water was added and the mixture was boiled with activated carbon, filtered while hot, and the filtrate cooled with ice. The resulting precipitate was filtered off and dried at 100°. The temperature during drying was raised gradually to avoid fusing of the precipitate. There was obtained 1.1 g (50%) of the precipitate of 2,6-diaminodiphensuccindane, which was colorless; m. p. 134-136°.

Found %: C 81.16, 81.21; H 6.80, 7.27; N 11.82, 11.70. $C_{16}H_{16}N_2$. Calculated %: C 81.32; H 6.83; N 11.86.

2,6-Dihydroxydiphensuccindane (III). A mixture of 0.45 g of 2,6-diaminodiphensuccindane, 280 ml of water and 1 ml of concentrated sulfuric acid was stirred at 50° until the precipitate dissolved. The solution was cooled to room temperature; a precipitate formed thereupon. This mixture was diazotized with a solution of 0.27 g of sodium nitrite in 15 ml of water until a positive test with starch-iodide paper remained for 40 min. The resulting solution was warmed for 1.5 hrs on a boiling water bath. The solution at first turned cloudy, then gave a precipitate. On the following day there was added to the reaction mixture 2.5 g of potassium hydroxide, the mixture was stirred at room temperature until the precipitate dissolved and the filtered solution was poured into a solution of dilute hydrochloric acid. The resulting flesh colored precipitate was filtered off and dried at 60°; weight, 0.42 g; m. p. 221-222°. The precipitate was dissolved with heating in 100 ml of benzene and the solution was boiled with carbon, after which the warm filtrate was diluted with 160 ml of petroleum ether. On the following day, the resulting precipitate was filtered off. The weight of the dry precipitate of 2,6-dihydroxydiphensuccindane was 0.25 g (59.5%); it was colorless and had m. p. 222-224°.

Found %: C 81.02, 80.80; H 5.84, 6.24. $C_{16}H_{14}O_2$. Calculated %: C 80.65; H 5.92.

Diphensuccindane (II). 80 g of zinc dust was stirred for 10 min with 20 ml of water and 40 ml of concentrated hydrochloric acid; the mixture was transferred into a long-necked 2-liter flask, the zinc dust was washed with water by decantation, then was shaken for 10 min with 80 ml of 5% solution of mercuric chloride and 4 ml of concentrated hydrochloric acid; the solution of mercuric chloride was then decanted and the amalgamated zinc was washed with water by decantation. Then 20 g of diphensuccindanedione was added to the flask, along with a solution of 700 ml of water and 80 ml of concentrated sulfuric acid and the flask contents were steam distilled over 16-18 hrs (with interruptions). The liquid volume in the reaction flask was maintained at 800-900 ml. The reaction product mainly settled on the condenser walls and was pushed out, as it accumulated, from the condenser by means of a piece of cotton and a rod. The steam distilled product contained an admixture of mercury droplets and some zinc; the last portions of the distilled product had a reddish brown color. After recrystallization from 110 ml of alcohol there was obtained 9.5 g (54%) of diphensuccindane which was colorless and had m. p. 100-102°. From the alcoholic mother liquor part of the alcohol was distilled until about 60 ml remained. On cooling, there formed an additional 2 g of precipitate with m. p. 99-100°.

Found %: C 93.30, 93.56; H 6.90, 6.87. $C_{16}H_{14}$. Calculated %: C 93.16; H 6.84.

SUMMARY

1. Diphensuccindane (by a new method) and 2,6-dihydroxydiphensuccindane were synthesized.

2. The estrogenic properties of 2,6-dihydroxydiphensuccindane and its open analog – p,p'-dihydroxy-2,3-diphenylbutane (meso form and racemate) were compared.

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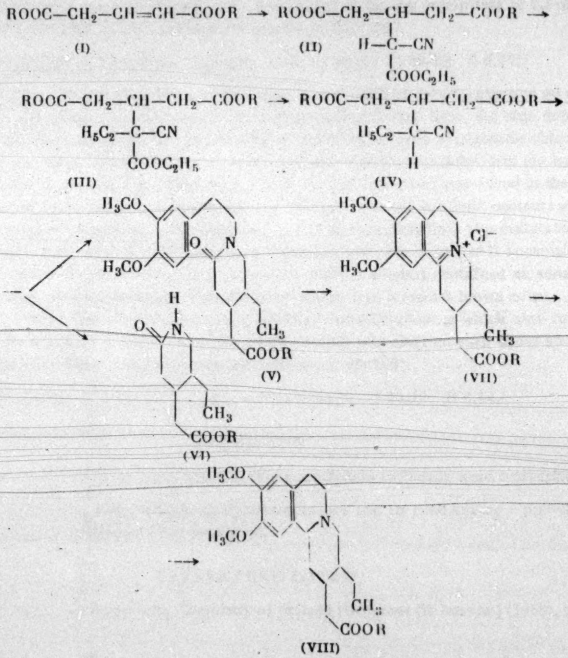
STUDIES IN THE SERIES OF ISOQUINOLINE COMPOUNDS

XIV. ESTERS OF ISOMERIC 4',5'-DIMETHOXY-6-ETHYL-3,4,5,6,7,8-HEXAHYDROBENZO-(1,2:1',2')-QUINOLIZYL-7-ACETIC ACIDS

R. P. Evstigneeva

In the present paper there is described the preparation of esters of isomeric 4',5'-dimethoxy-6-ethyl-3,4,5,6,7,8-hexahydrobenzo-(1,2:1',2')-quinolizyl-7-acetic acids which are important intermediates in the synthesis of isomeric emetines.

The synthesis was accomplished according to one [1] of the schemes previously suggested by us [2].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(I)
ROOC—CH₂—CH—CH₂—COOR
H—C—CN
COOC₂H₅
(II)
ROOC—CH₂—CH—CH₂—COOR
H₅C₂—C—CN
COOC₂H₅
(III)
ROOC—CH₂—CH—CH₂—COOR
H₅C₂—C—CN
H
(IV)
H₃CO
H₃CO
O
N
CH₃
COOR
(V)
H
O
N
CH₃
COOR
(VI)
H₃CO
H₃CO
N⁺
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CH₃
COOR
(VII)
H₃CO
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CH₃
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(VIII)

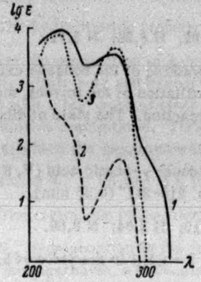

Fig. 1. Ultraviolet absorption spectra in ethyl alcohol. 1) Ethyl ester of N-[β-(3',4'-dimethoxyphenyl)-ethyl]-δ-ethyl-α-piperidone-γ-acetic acid; 2) ethyl ester of δ-ethyl-α-piperidone-γ-acetic acid; 3) dihomoveratrylamine.

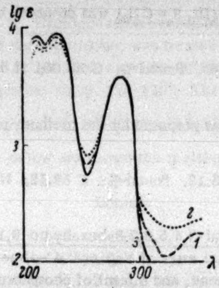

Fig. 2. Ultraviolet absorption spectra of hydrochlorides of ethyl esters of isomeric 4',5'-dimethoxy-6-ethyl-3,4,5,6,7,8-hexahydrobenzo-(1,2:1',2')-quinolizyl-7-acetic acids in ethyl alcohol. Numbers of curves correspond to numbers of the isomers.

In the course of the synthesis there was prepared a series of esters of β-substituted glutaric acids (II-IV, R = CH_3).

The condensation of β-(α'-cyano)-propylglutaric acid (IV) with homoveratrylamine was studied in detail. Along with the main reaction product – the ester of N-[β-(3',4'-dimethoxyphenyl)-ethyl]-δ-ethyl-α-piperidone-γ-acetic acid (V) there were isolated the following by-products: 1) ester of δ-ethyl-α-piperidone-γ-acetic acid (VI) and 2) dihomoveratrylamine. The compounds prepared in this step have different ultraviolet absorption characteristics (Fig. 1).

The ester of N-[β-(3',4'-dimethoxyphenyl)-ethyl]-δ-ethyl-α-piperidone-γ-acetic acid (V) may exist in principle in two isomeric forms; however, all our attempts to isolate a second isomer failed. Evidently, the substituent on the nitrogen aids the predominant formation of but one stereoisomer. According to the information gained from conformational analysis, the most advantageous structure for the substituted piperidone is the trans-form with equatorial substituents. The by-product, the ester of δ-ethyl-α-piperidone-γ-acetic acid which does not have any substituents at the nitrogen, is obtained under these conditions in two stereoisomeric forms: 1) crystalline cis-isomer, m. p. 84-85° and 2) liquid trans-isomer, b. p. 175-176° (1.5 mm).

The ester of N-[β-(3',4'-dimethoxyphenyl)-ethyl]-δ-ethyl-α-piperidone-γ-acetic acid is transformed by the action of phosphorus oxychloride into the derivative of quinolizine. The resulting salt of the quaternary base (VII) yields on reduction the ester of 4',5'-dimethoxy-6-ethyl-3,4,5,6,7,8-hexahydrobenzo-(1,2:1',2')-quinolizyl-7-acetic acid (VIII). Hydrogenation of the chloride of the quaternary base proceeds stereospecifically, depending on the catalyst used and on the pH of the medium. As a result of this reaction there were isolated three compounds: 1) the isomer obtained during hydrogenation in the presence of platinum oxide in acid medium, 2) the isomer obtained during hydrogenation in the presence of platinum oxide in neutral medium, and 3) the isomer obtained in hydrogenation in the presence of Raney nickel in neutral medium.

In the case of hydrogenation with nickel with heating, isomerization evidently occurs. The resulting isomers are very close to each other in their properties but do display a depression in mixed melting points of their hydrochlorides. The isomers have almost coincident ultraviolet absorption spectra (Fig. 2).

EXPERIMENTAL

I. Ethyl ester of N-[β-(3',4'-dimethoxyphenyl)-ethyl]-δ-ethyl-α-piperidone-γ-acetic acid (V, R = C_2H_5). Ethyl ester of β-(α'-cyano)-propylglutaric acid (10.42 g) and 48 g of homoveratrylamine in 50 ml of anhydrous ethyl alcohol were hydrogenated in the presence of 4 g of Raney nickel at 110 atmos and 110-115° for 1 hr. The catalyst was filtered off and the alcohol was distilled in vacuum. The residue was dissolved in benzene and washed with 3% hydrochloric acid, then with a sodium bicarbonate solution. After distillation of the solvent, the residue was distilled.

1st fraction. Ethyl ester of δ-ethyl-α-piperidone-γ-acetic acid (VI, R = C_2H_5). Yield: 0.75 g (8.66%). B. p. 169-170° (1 mm).

Found %: C 61.80; H 9.06; N 6.73. $C_{11}H_{19}O_3N$. Calculated %: C 61.95; H 8.98; N 6.57.

2nd fraction. Ethyl ester of N-[β-(3',4'-dimethoxyphenyl)-ethyl]-δ-ethyl-α-piperidone-γ-acetic acid (V, R = C_2H_5). Yield: 5.25 g (34.2%). B. p. 200.5-202.5° (0.15 mm).

Found %: C 66.79; H 8.26; N 3.77. $C_{21}H_{31}O_5N$. Calculated %: C 66.82; H 8.28; N 3.71.

Isolation of amines. The hydrochloric acid solution, obtained after the washing of the benzene extract of piperidones, was neutralized with alkali and extracted with benzene. After distillation of the solvent, the residue was distilled. There was obtained 33.6 g of homoveratrylamine taken for the reaction. The yield of dihomoveratrylamine was 2.74 g (6%). B. p. 198-205° (0.2 mm), m. p. 53.5-54°.

Methyl ester of N-[β-(3',4'-dimethoxyphenyl)-ethyl]-δ-ethyl-α-piperidone-γ-acetic acid (V, R = CH_3) was prepared analogously to the corresponding ethyl ester. Yield: 43.7%. B. p. 210-211° (0.35 mm).

Found %: C 65.80; H 7.91; N 4.11. $C_{20}H_{29}O_5N$. Calculated %: C 66.10; H 8.04; N 3.85.

As a by-product there was also obtained the unalkylated piperidone (VI, R = CH_3) in the yield of 5.71%. B. p. 112-115° (0.35 mm).

Found %: N 7.30. $C_{10}H_{17}O_3N$. Calculated %: N 7.02.

II. Methyl ester of β-(cyanocarbethoxy)-methylglutaric acid (II, R = CH_3) was obtained by the previously described method for the corresponding ethyl ester [1]. Yield: 82%.

B. p. 157-159° (2 mm), d_4^{20} 1.1825, $n^{20}D$ 1.4588, MR_D 62.68; calc. 62.39. Found %: C 52.99; H 6.50; N 5.22. $C_{12}H_{17}O_6N$. Calculated %: C 53.13; H 6.31; N 5.16.

III. Methyl ester of β-(α'-cyano-α'-carbethoxy)-propylglutaric acid (III, R = CH_3) was prepared by the previously described method [1]. Yield: 86.5%.

B. p. 156-158° (1 mm), d_4^{20} 1.1817, $n^{20}D$ 1.4780, MR_D 71.69; calc. 71.63. Found %: C 55.06; H 6.99; N 4.50. $C_{14}H_{21}O_6N$. Calculated %: C 56.18; H 7.07; N 4.69.

IV. Methyl ester of β-(α'-cyano)-propylglutaric acid (IV, R = CH_3) was prepared by the method, previously described for the ethyl ester [1]. The yield was 38%.

B. p. 126.5-127° (1 mm), d_4^{20} 1.0912, $n^{20}D$ 1.4506, MR_D 56.00; calc. 56.12. Found %: C 58.12; H 7.56; N 6.29. $C_{11}H_{17}O_4N$. Calculated %: C 58.13; H 7.56; N 6.16.

V. Chloride of quaternary base of ethyl ester of 4',5'-dimethoxy-6-ethyl-3,4,5,6,7,8-hexahydro-9,10-dehydrobenzo-(1,2:1',2')-quinolizyl-7-acetic acid (VII, R = C_2H_5). 1 g of ethyl ester of N-[β-(3',4'-dimethoxyphenyl)-ethyl]-δ-ethyl-α-piperidone-γ-acetic acid, 6 ml of anhydrous toluene, and 5.5 ml of phosphorus oxychloride were heated at gentle reflux for 1 hr. The toluene and excess phosphorus oxychloride were distilled off in vacuo. The residue was washed with 50 ml of absolute ether and was then dissolved in 10 ml of 6% hydrochloric acid. The solution was evaporated in vacuo at 25-30°. Complete removal of moisture was achieved by addition of anhydrous ethyl alcohol (5 ml, 3 times) to the residue and a subsequent distillation of it in vacuo. The residual red-yellow oil was the chloride of the quaternary base of the ethyl ester of 4',5'-dimethoxy-6-ethyl-3,4,5,6,7,8-hexahydro-9,10-dehydrobenzo-(1,2:1',2')-quinolizyl-7-acetic acid mixed with phosphoric acid.

VI. Ethyl esters of 4',5'-dimethoxy-6-ethyl-3,4,5,6,7,8-hexahydrobenzo-(1,2:1',2')-quinolizyl-7-acetic acids (VIII, R = C_2H_5). 1. Hydrogenation in the presence of platinum oxide in acid medium. The crude chloride, prepared from 1 g of the piperidone, was dissolved in 7 ml of anhydrous ethyl alcohol and hydrogenated in the presence of 0.2 g of platinum oxide under 80 atmos for 4 hrs. The catalyst was filtered off and the alcohol was distilled off in vacuo. 10 ml of water was added to the residue. The solution was shaken with 20 ml of ether, then neutralized, with cooling, by means of aqueous ammonia. The separated oil was extracted with 50 ml of ether. The extract was washed with 10 ml of 5% aqueous alkali and dried with sodium sulfate. The base was a light yellow oil, readily soluble in the usual organic solvents and insoluble in water. The yield: 0.72 g (74.9%, calculated on the piperidone). The base distilled at 0.1 mm and the temperature of the air bath of 290-300°.

Found %: C 69.58; H 8.50; N 4.01. $C_{21}H_{31}O_4N$. Calculated %: C 69.78; H 8.65; N 3.87.

The hydrochloride was obtained in amorphous form by treatment of the ethereal solution of the base with ether containing hydrogen chloride. From the undistilled base, the hydrochloride separates in the form of a colorless amorphous substance, readily soluble in water and alcohol and insoluble in ether. It was very hygroscopic.

Found %: C 63.68; H 8.31; N 3.61. $C_{21}H_{32}O_4NCl$. Calculated %: C 63.38; H 8.11; N 3.52.

The hydrochloride prepared from distilled base was also amorphous and hygroscopic. M. p. 157-157.5°.

For the preparation of a crystalline hydrochloride, 0.5 g of the crude base ester was dissolved in 5 ml of 3% hydrochloric acid and evaporated in vacuo. The residue was taken up in the least volume of alcohol and treated with a few drops of ether until a slight cloudiness appeared. After a prolonged standing, the crystalline hydrochloride precipitated. Yield: 0.4 g. M. p. 196°. The hydrochloride crystallized with 1.5 molecule of water, owing to which the specimen was dried, prior to analysis, in vacuo at 110° for 1.5 hr.

Found %: C 63.40; H 8.19; N 3.78. $C_{21}H_{32}O_4NCl$. Calculated %: C 63.38; H 8.11; N 3.52.

The crystalline hydrochloride from the distilled base had m. p. 158-168°.

2. Hydrogenation in the presence of platinum oxide in neutral medium. The crude chloride, prepared from 1 g of the piperidone, was dissolved in 5 ml of anhydrous alcohol and neutralized with alcoholic solution of ammonia until the acid reaction to Congo red disappeared. The precipitate was separated and the filtrate was evaporated in vacuo. The residue was dissolved in 10 ml of anhydrous alcohol and subjected to hydrogenation at 110 atmos. After the usual treatment there was obtained 0.75 g (78.5%, based on piperidone) of the product. The hydrochloride was amorphous and had m. p. 171.5-173.5°. The crystalline hydrochloride was isolated analogously to the method described in the previous experiment; it gave colorless thin plates which formed rosettes. M. p. 194-196°. The substance was dried for 1.5 hr at 110° (1 mm) prior to the analysis.

Found %: C 63.54; H 8.16; N 3.59. $C_{21}H_{32}O_4NCl$. Calculated %: C 63.38; H 8.11; N 3.52.

3. Hydrogenation over Raney nickel. The chloride of quaternary base of the quinolizine, prepared from 2 g of the piperidone, was treated as in the previous experiment and hydrogenated in the presence of 1 g of Raney nickel at 100 atmos and 85-90° for 2 hrs. Yield: 0.95 g (49.6% based on the piperidone). The hydrochloride was amorphous; m. p. 175-179°. The crystalline hydrochloride formed thin colorless plates; m. p. 193.5-194.8°.

Found %: C 63.45; H 7.90; N 3.53. $C_{21}H_{32}O_4NCl$. Calculated %: C 63.38; H 8.11; N 3.52.

Below are shown the melting points of mixed samples of the isomers:

Isomers	Amorphous hydrochlorides	Crystalline hydrates
1 and 2	164.5-165.5°	178-180°
1 and 3	155-156°	155-168°
2 and 3	167-167.5°	164-185°

Methyl ester of 4',5'-dimethoxy-6-ethyl-3,4,5,6,7,8-hexahydrobenzo-(1,2:1',2')-quinolizyl-7-acetic acid (VIII, R = CH_3) was isolated in 86.4% yield in the case of hydrogenation over Raney nickel catalyst. The amorphous hydrochloride had m. p. 186-187°. The crystalline hydrochloride was isolated in the form of irregular polyhedrons. M. p. 195-195.5°. The specimen was dried prior to analysis at 110° (1 mm) for 1.5 hr.

Found %: C 62.55; H7.90; N 3.66. $C_{20}H_{30}O_4NCl$. Calculated %: C 62.54; H 7.88; N 3.65.

SUMMARY

1. The synthesis of esters of isomeric 4',5'-dimethoxy-6-ethyl-3,4,5,6,7,8-hexahydrobenzo-(1,2:1',2')-quinolizyl-7-acetic acid was realized.

2. The reaction of condensation of methyl and ethyl esters of β-(α'-cyano)-propylglutaric acid with homoveratrylamine was studied.

3. The conditions for sterically directed hydrogenation of the quaternary chloride of the ester of 4',5'-dimethoxy-6-ethyl-3,4,5,6,7,8-hexahydro-9,10-dehydro-benzo-(1,2:1',2')-quinolizyl-7-acetic acid were worked out.

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* Original Russian pagination. See C. B. translation.

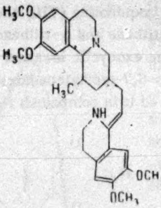
STUDIES IN THE SERIES OF ISOQUINOLINE COMPOUNDS

XV. SYNTHESIS OF ISOMERIC o-METHYLPSYCHOTRINES

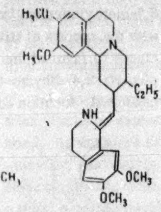
R. P. Evstigneeva, R. G. Glushkov, and N. A. Preobrazhenskii

The alkaloid o-methylpsychotrine is isolated along with emetine from the roots of the tropical ipecacuanha plant. During the study of the alkaloids of this group the major attention was devoted to emetine since it possesses some valuable therapeutic properties and is contained in the plant in predominant amounts. The structure of emetine was established in 1949 [1-5] and confirmed by synthesis in 1950 [6]. The remaining ipecacuanha alkaloids have been studied less intensively and the structures of the majority of them have not been proved finally.

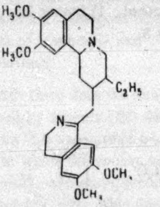
o-Methylpsychotrine was discovered only in 1917, considerably later than other alkaloids of this group. In its elemental composition o-methylpsychotrine differs from emetine only by a lesser content of hydrogen, by two atoms, and may be obtained from the latter by oxidation with mercuric acetate. o-Methylpsychotrine has been described as a secondary-tertiary base since it yields a singly substituted N-benzoyl derivative on being heated with benzoic anhydride. Formula (I) was suggested in 1927 for o-methylpsychotrine in accord with one of the structures proposed for emetine [7].



(I)



(II)

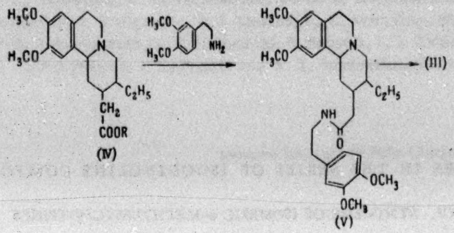


(III)

The position of the double bond was confirmed by the fact that in the oxidation of N-benzoyl-o-methylpsychotrine with perphthalic acid and ozone there is obtained N-benzoylcoridaldine [8]. In 1949, following the establishment of emetine structure, formula (II) was accepted for o-methylpsychotrine. However, a little later a conclusion was drawn concerning the 1,2-position of the double bond in the dihydroisoquinoline ring (III) [9], on the basis of the study of the ultraviolet absorption spectrum of o-methylpsychotrine oxalate. However, this supposition is poorly compatible with the secondary-tertiary character of the base. Thus, the problem of the structure of o-methylpsychotrine remained open.

The scheme of emetine synthesis developed by us gave the opportunity to prepare o-methylpsychotrine as well. Stereoisomeric ethers of quinolizine (1-3) [17] were employed for this purpose (see diagram at top of next page).

Amides (V), which were close to each other in properties, were prepared by heating the esters (IV) with homoveratrylamine at 180-200°. The ultraviolet absorption maxima of these amides lie at the same wavelength (Fig. 1). The amides were converted into isoquinoline derivatives, which had the composition and the structure which corresponded to the alkaloid o-methylpsychotrine, the reaction being performed by the action of phosphorus



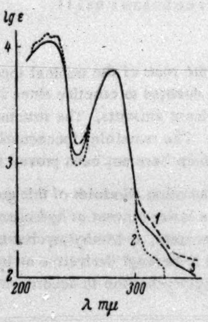
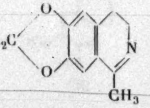


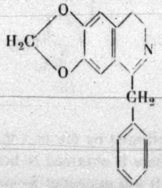
Fig. 1. Ultraviolet absorption spectra of the amides in ethyl alcohol. 1) Isomer 1; 2) isomer 2; 3) isomer 3.

oxychloride in chloroform solution. The bases were isolated in an amorphous state and had very close melting points. They were unstable to atmospheric oxygen and sunlight. Their oxalates were obtained in the form of crystalline hydrates which were readily recrystallized from methyl alcohol and lost water only after being dried at 110° and 1 mm for 3 hrs. The melting points of the oxalates were close to each other. The mixed melting points showed small but clear depressions. The (+)-tartrates were also prepared; these crystallize without water of crystallization.

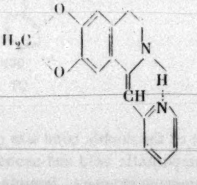
The problem of the location of the double bond in 3,4-dihydroisoquinoline ring remains unclear not only for o-methylpsychotrine but also for the entire group of similar compounds. On the basis of a study of the ultraviolet absorption spectra of 1-methyl-3,4-dihydro-6,7-methylenedioxyisoquinoline (VI), 1-benzyl-3,4-dihydro-6,7-methylenedioxyisoquinoline (VII) and 1-(α-picolyl)-3,4-dihydro-6,7-methylenedioxyisoquinoline (VIII) and the comparison of these with the spectra of stilbene and α-stilbazole Bills and Noller [10] concluded in favor of the exocyclic location of the double bond in 1-(α-picolyl)-3,4-dihydro-6,7-methylenedioxyisoquinoline (VIII) and the endocyclic location of it in compounds (VI) and (VII).



(VI)



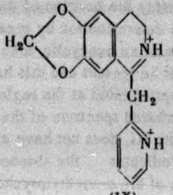
(VII)



(VIII)

The character of the absorption curve changes in passing from the base (VIII) to the hydrochloride (IX), which fact is evidently connected with the translocation of the double bond. The exocyclic structure of compound (VIII) is explained, most probably, by the possibility of an intramolecular hydrogen bond (see diagram at top of next page).

This supposition is confirmed by the fact that 1-(β-picolyl)-3,4-dihydro-6,7-methylenedioxyisoquinoline, in which an intramolecular hydrogen bond cannot exist, has an endocyclic N=C double bond, as shown by the absorption spectrum and by transformation of compound (X) into the isoquinoline derivative (XI). 1-(α-Picolyl)-3,4-dihydro-6,7-methylenedioxyisoquinoline (VIII) does not yield an isoquinoline derivative.



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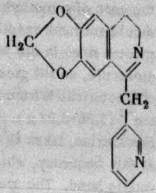
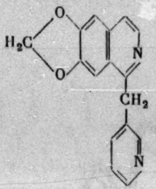


(X)



(XI)

It is possible to conclude, on the basis of these studies, that for the 1-substituted 3,4-dihydroisoquinoline compounds the endocyclic location of the double bond is more common and that only in a few cases is the exocyclic disposition of the double bond possible.

Openshaw and Wood [9], in comparing the ultraviolet absorption spectra of the oxalate of natural o-methylpsychotrine with the spectrum of the hydrochloride of 1-methyl-3,4-dihydro-6,7-methylenedioxyisoquinoline, came to the conclusion of the endocyclic location of the double bond in o-methylpsychotrine. Although this position is correct in the final result, it could not be deduced solely on the basis of the spectrum of the salt. The spectroscopic study of the base was also necessary since the salt and the base might have different dispositions of the double bond.

We determined the ultraviolet spectra of the oxalates of the stereoisomeric synthetic o-methylpsychotrines (Fig. 2). The absorption curves of all three isomers coincide almost completely and are similar to the absorption curve of the oxalate of natural o-methylpsychotrine. The same is observed for the ultraviolet spectra of (+)-tartrates of o-methylpsychotrines (Figs. 2 and 3). We also examined the ultraviolet spectra of the stereoisomeric bases of o-methylpsychotrine isolated from the purified oxalates (Fig. 4). The absorption curves of the bases are similar to each other and are analogous in the maximum distribution to the absorption curves of 1-methyl- and 1-benzyl-3,4-dihydro-6,7-methylenedioxyisoquinolines.

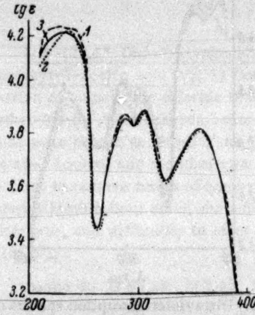


Fig. 2. Ultraviolet absorption spectra of oxalates of o-methylpsychotrines in ethyl alcohol. 1) Isomer 1; 2) isomer 2; 3) isomer 3.

In accordance with these data the structure of o-methylpsychotrine should be expressed by formula (III) with the endocyclic double bond. At the same time it is known that o-methylpsychotrine yields monoacyl derivatives in which the double bond can be only exocyclic. N-Benzoyl- and N-succinyl-o-methylpsychotrines, prepared from natural o-methylpsychotrine, have been described in the literature. We prepared N-acetyl derivatives of stereoisomeric o-methylpsychotrines by treatment of the ethereal solutions of the bases with acetic anhydride and aqueous alkali. The bases were isolated in an amorphous state but yielded crystalline oxalates. The melting points of the bases of N-acetyl-o-methylpsychotrines were close to the corresponding melting points of the bases of o-methylpsychotrine. However, the bases of N-acetyl-o-methylpsychotrine were more stable to the action of light, atmospheric oxygen and other external effects. If one dissolves the base of o-methylpsychotrine in carbon tetrachloride, the solution begins to cloud in a few minutes and a red precipitate forms; m. p. 171-178° (deforms at 164°). This resembles rubremetine chloride (m. p. 166-173°) in its appearance. A similar picture is not observed in a solution of N-acetyl-o-methylpsychotrine in carbon tetrachloride. The solution remains transparent for many days. The melting points of oxalates of N-acetyl-o-methylpsychotrines are also close to the corresponding melting points of oxalates of o-methylpsychotrines, but show a depression in mixed melting points with them. The ultraviolet spectra of bases of N-acetyl-o-methylpsychotrines (Fig. 5) and their oxalates (Fig. 6) turned out to be analogous to the corresponding spectra of o-methylpsychotrines. The same picture was observed in the case of 1-benzal-1,2,3,4-tetrahydro-2-methyl-6,7-methylenedioxyisoquinoline (XII). Therefore, the ultraviolet spectra are insufficiently dependable for the determination of the position of the double bond.

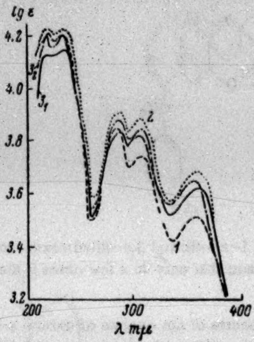


Fig. 3. Ultraviolet absorption spectra of (+)-tartrates of o-methylpsychotrines in ethyl alcohol. 1) Isomer 1; 2) isomer 2; 3_1) isomer 3; 3_2) isomer 3 from mother liquor.

Infrared spectroscopy gives better results in many cases. In the case of o-methylpsychotrine the position of the double bond should succumb readily to a determination by means of infrared spectra since in the presence of an exocyclic double bond in the molecule, an NH group must be present and this has a definite, characteristic infrared absorption band at the region of 3500-3100 cm^{-1} (2.86-3.23 μ). The infrared spectrum of the base of o-methylpsychotrine, taken in vaseline oil, does not have any absorption bands at this frequency, which indicates the absence of an exocyclic double bond. The spectrum of the o-methylpsychotrine base in carbon tetrachloride also showed the absence of the NH group. We were obliged to omit taking the spectrum in a polyfluorocarbon, which is usually used for working in this region of the spectrum, since o-methylpsychotrine reacted instantly with this substance with formation of a red color. For comparison there was taken the spectrum of a standard substance – dihomoveratrylamine – at the same concentration. In this there was present the band of the NH group at 3293.5 cm^{-1}. The location of this band indicates that in this compound there is an intramolecular hydrogen bond.

Replacement of hydrogen by deuterium is often used in the study of the hydrogen bond, since this change is accompanied by a sharp displacement of the characteristic frequency to the side of longer wavelengths. We attempted to use this method of study in the hopes of locating the NH group in o-methylpsychotrine. It is known that deutero-hydrogen exchange in the alcohol and the amino groups occurs extraordinarily rapidly [11, 12], while the exchange of hydrogen bound to carbon either does not proceed at all or requires special conditions [13, 14]. The base of o-methylpsychotrine was dissolved in dry dioxane and treated with excess heavy water. After 2 days' standing the base was isolated and subjected to spectroscopic examination. The ND band also failed to be found, which indicates the absence of an exocyclic bond in o-methylpsychotrine. The deutero-hydrogen exchange failed to take place in the case of dihomoveratrylamine as well. This agrees with other known facts about the hindered hydrogen exchange at the hydrogen which participates in the formation of an intramolecular hydrogen bond. For example, hydrogen is not exchanged in 1-hydroxyanthraquinone [15] or 1-benzeneazo-2-naphthylamine [16]. In di-

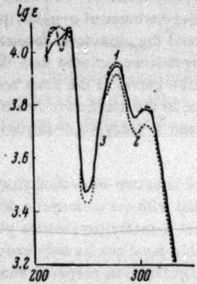


Fig. 4. Ultraviolet absorption spectra of bases of o-methylpsychotrine in ethyl alcohol. 1) Isomer 1; 2) isomer 2; 3) isomer 3.

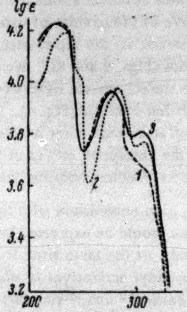


Fig. 5. Ultraviolet absorption spectra of bases of N-acetyl-o-methylpsychotrines in ethyl alcohol. 1) Isomer 1; 2) isomer 2; 3) isomer 3.

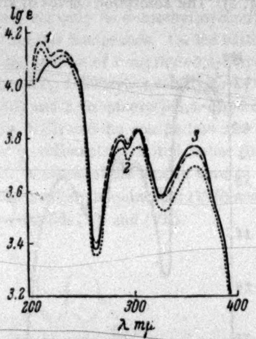
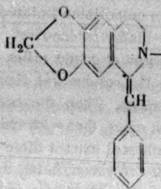
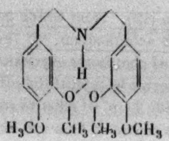


Fig. 6. Ultraviolet absorption spectra of oxalates of N-acetyl-o-methylpsychotrines in ethyl alcohol. 1) Isomer 1; 2) isomer 2; 3) isomer 3.

homoveratrylamine, evidently, the oxygen of the methoxyl group, located in meta position in respect to the side chain (XIII), participates in the formation of the hydrogen bond.



(XII)



(XIII)

Thus, the infrared spectra of the base of o-methylpsychotrine confirm the presence in it of an endocyclic double bond. The spectroscopic study of salts of o-methylpsychotrine is extraordinarily complicated by the presence of water of crystallization in them. However, on the basis of the spectral data in the region of 1200-1700 cm^{-1}, it is possible to say sufficiently confidently that the salt is devoid of an NH group.

Summarizing all the above-said, we should consider that the structure of o-methylpsychotrine corresponds to formula (III). The formation of the mono-N-acyl derivatives may be explained by the presence of tautomerism between (II) and (III) with the predominant shift in the direction of the compound with endocyclic double bond (III). Such a shift of equilibrium in the direction of one of the possible forms is observed in neutral and acidic solutions of compounds capable of ketimide-enamine transformations. The exocyclic disposition of the double bond arises only under the action of alkali and is fixed by an acylating agent.

EXPERIMENTAL

I. β-(3",4"-Dimethoxyphenyl)-ethylamide of 4',5'-dimethoxy-6-ethyl-3,4,5,6,7,8-hexahydrobenzo-(1,2:1',2')-quinolizyl-7-acetic acid (V). 1) From quinolizine prepared in cyclization with phosphorus oxychloride and hydrogenation of quinolizine chloride in the presence of platinum oxide in acid medium. Ethyl ester of 4',5'-dimethoxy-6-ethyl-3,4,5,6,7,8-hexahydrobenzo-(1,2:1',2')-quinolizyl-7-acetic acid (IV) (0.72 g) and 1 g of homoveratrylamine were heated at 180-200° for 7 hrs in a nitrogen stream. 20 ml of dry ether was added to the reaction mixture after cooling and the whole was left overnight. Then, the solid amide was filtered off, washed with water on the filter to remove traces of homoveratrylamine, and dried in a desiccator. The yield was 0.6 g (60.2%). After recrystallization from ether, the amide formed a colorless crystalline substance, readily soluble in alcohol and chloroform, and difficultly in ether and petroleum ether, and insoluble in water; m. p. 144-145° (deforms slightly at 136.5°).

Found %: C 69.88; H 8.09; N 5.66, 5.68. $C_{29}H_{40}O_5N_2$. Calculated %: C 70.13; H 8.12; N 5.64.

2) From quinolizine prepared by cyclization of piperidone with phosphorus oxychloride and hydrogenation in the presence of platinum oxide in neutral medium. From 0.88 g of ethyl ester of 4',5'-dimethoxy-6-ethyl-3,4,5,6,7,8-hexahydrobenzo-(1,2:1',2')-quinolizyl-7-acetic acid (IV) and 1 g of homoveratrylamine there was obtained 0.7 g (57.8%) of the amide, under the same conditions as in the previous experiment. The product was isolated from ether in the form of colorless crystals which were readily soluble in alcohol, chloroform and acetone, difficultly in ether, and petroleum ether, and insoluble in water. M. p. 147.5-148.5° (deforms at 145.5°).

Found %: C 70.06, 70.04; H 7.89, 7.92; N 5.75, 5.74. $C_{29}H_{40}O_5N_2$. Calculated %: C 70.13; H 8.12; N 5.64.

3) From quinolizine prepared by cyclization of piperidone with phosphorus oxychloride and hydrogenation in the presence of Raney nickel catalyst. From 3 g of methyl ester of 4',5'-dimethoxy-6-ethyl-3,4,5,6,7,8-hexahydrobenzo-(1,2:1',2')-quinolizyl-7-acetic acid (IV) and 3 g of homoveratrylamine, under the above-described conditions, there was obtained 2.6 g of the amide (60.5%). This separated in the form of colorless crystals from a mixture of anhydrous ethyl alcohol and petroleum ether (1:2). It was readily soluble in alcohol and chloroform, difficultly in benzene, toluene, ether and petroleum ether, and insoluble in water. M. p. 144-146.5° (deforms at 139°).

Found %: C 70.42, 70.25; H 8.37, 8.04; N 5.68, 5.76. $C_{29}H_{40}O_5N_2$. Calculated %: C 70.13; H 8.12; N 5.64.

II. o-Methylpsychotrine (III). From amide prepared from quinolizine isolated after hydrogenation in the presence of platinum oxide in acid medium. a) The base of o-methylpsychotrine. The amide (1.6 g), 15 ml of dry chloroform and 10 ml of phosphorus oxychloride were heated at gentle reflux for 4 hrs. The chloroform and excess phosphorus oxychloride were distilled off in vacuo. The residue was dissolved in 10 ml of 5% hydrochloric acid and extracted with 20 ml of ether to remove impurities. Then the cooled aqueous solution was made alkaline with ammonia. The separated base was extracted with ether, then with chloroform. The solvents were distilled off after drying with potassium carbonate. From the ethereal extract there was obtained 0.45 g of the base in the form of a slightly yellow oil, which rapidly solidified in vacuo, being transformed into a foam-like colorless amorphous substance. After removal of ether in vacuo, from a solution in dry ether of the residue obtained after evaporation of the solvent from the chloroform extract above, there was obtained an additional 0.5 g of the o-methylpsychotrine base. The yield was 0.95 g (61.6%). M. p. 59-60° (deforms at 52.5°).

b) Oxalate of o-methylpsychotrine was prepared by treatment of an ethereal solution of the base with an ethereal solution of oxalic acid. The oxalate attracts atmospheric moisture during filtration. After three recrystallizations from anhydrous methyl alcohol, the oxalate formed a colorless substance which was readily soluble in water, difficultly in alcohol and insoluble in ether. The substance was dried at 110° (1 mm) for 3 hrs prior to analysis for carbon and hydrogen. M. p. 147.5° (it deforms at 145.5-146.5°).

Found %: C 60.13; H 6.23; N 4.40. $C_{33}H_{42}N_2O_{12}$. Calculated %: C 60.17; H 6.43; N 4.25.

c) Base of o-methylpsychotrine was isolated from the oxalate. The 0.15 g of o-methylpsychotrine oxalate obtained above was dissolved in water and treated with ammonia. The separated base was extracted with ether and dried over anhydrous potassium carbonate. The base, after the distillation of ether, was isolated in the form of a colorless amorphous substance, readily soluble in organic solvents and insoluble in water. Yield was 0.1 g (79.5°). M. p. 59-60° (it deforms at 52.5°).

Found %: C 72.80; H 8.25; N 5.80. $C_{29}H_{38}O_4N_2$. Calculated %: C 72.77; H 8.00; N 5.85.

d) (+)-Tartrate of o-methylpsychotrine. To a solution of 0.2 g of the o-methylpsychotrine base in 2 ml of anhydrous ethyl alcohol there was added a solution of 0.15 g of (+)-tartaric acid in 4 ml of alcohol. A precipitate of (+)-tartrate precipitated immediately and was filtered off. The yield was 0.3 g (88%). The (+)-tartrate (0.3 g) was recrystallized from 5 ml of anhydrous ethyl alcohol. There was obtained 0.2 g of the product. After repeated recrystallization from 6 ml of alcohol, there was isolated 0.13 g of slightly yellowish substance, readily soluble in water, moderately in alcohol and acetone, and insoluble in ether. M. p. 125° (with decomposition) (deforms at 100°); $[\alpha]^{18}D$ +17.8° (c 3.4; water).

Found %: C 57.06; H 6.86; N 3.83, 3.86. $C_{29}H_{38}O_4N_2 \cdot 2C_4H_6O_6$. Calculated %: C 57.07; H 6.47; N 3.59.

2) From the amide prepared from quinolizine isolated after hydrogenation in the presence of platinum oxide in neutral medium. a) Base of o-methylpsychotrine. From 1.5 g of the amide there was obtained as a result of treatment analogous to that described above, 1.31 g (91%) of o-methylpsychotrine base in the form of a colorless amorphous substance. M. p. 50° (deforms at 40°).

b) The oxalate was prepared by the reaction of the base with oxalic acid in ethereal solution. The oxalate precipitate was filtered off and recrystallized 3 times from anhydrous methyl alcohol. The substance was dried at 110° (1 mm) for 3 hrs prior to analysis for carbon and hydrogen. M. p. 148° (decomp.) (deforms at 146.5°).

Found %: C 59.96, 60.21; H 6.57, 6.71; N 4.40, 4.22. $C_{33}H_{42}O_{12}N_2$. Calculated %: C 60.17; H 6.43; N 4.25.

c) o-Methylpsychotrine base isolated from the oxalate. From 0.15 g of the oxalate there was obtained 0.12 g (79.5%) of the base. M. p. 58-59° (deforms at 50°).

Found %: C 72.40; H 8.13; N 5.57. $C_{29}H_{38}O_4N_2$. Calculated %: C 72.77; H 8.00; N 5.85.

d) (+)-Tartrate of o-methylpsychotrine. The o-methylpsychotrine base (0.21 g) was dissolved in 3 ml of anhydrous ethyl alcohol and treated with 0.2 g of (+)-tartaric acid in 4 ml of alcohol. The precipitate of (+)-tartrate was recrystallized from 9 ml of anhydrous ethyl alcohol. There was obtained 0.1 g of product. After repeated crystallization from 4.5 ml of alcohol there was isolated 50 mg of the product. (+)-Tartrate forms a slightly yellowish substance, readily soluble in water, moderately in alcohol/and acetone and insoluble in ether. M. p. 125° (decomp.); $[\alpha]^{18}D$ +11.45° (c 4.66; water).

Found %: C 57.11; H 6.71; N 3.87, 3.60. $C_{29}H_{38}O_4N_2 \cdot 2C_4H_6O_6$. Calculated %: C 57.07; H 6.47; N 3.59.

3) From the amide prepared from quinolizine isolated after hydrogenation in the presence of Raney nickel catalyst. a) From 2.3 g of the amide there was obtained by the above-described method 2 g (91%) of the base in the form of colorless amorphous substance, readily soluble in alcohol and chloroform, difficultly in ether and insoluble in water. M. p. 60-61° (deforms at 38°).

b) o-Methylpsychotrine oxalate – a colorless crystalline substance, readily soluble in water, difficultly in alcohol and insoluble in ether. It was purified by three recrystallizations from anhydrous methyl alcohol. The substance was dried at 1 mm and 110° for 3 hrs prior to analysis. M. p. 147.5° (decomp.) (deforms at 145.5°).

Found %: C 60.31, 59.86; H 6.34, 6.41; N 4.40, 4.28. $C_{33}H_{42}O_{12}N_2$. Calculated %: C 60.17; H 6.43; N 4.25.

c) Base of o-methylpsychotrine isolated from the oxalate. From 0.15 g of the oxalate there was obtained 0.084 g (66.79%) of the base in the form of a colorless amorphous substance, readily soluble in alcohol and chloroform, difficultly in ether and insoluble in water. M. p. 58-59° (deforms at 50°).

Found %: C 72.53; H 8.32; N 5.77. $C_{28}H_{38}O_4N_2$. Calculated %: C 72.77; H 8.00; N 5.85.

d) (+)-Tartrate of o-methylpsychotrine. To 50 mg of the o-methylpsychotrine base in 2 ml of anhydrous ethyl alcohol there was added 31 mg of (+)-tartaric acid in 2 ml of alcohol. The resulting precipitate was filtered off. The yield was 40 mg (50%). M. p. 159° (decomp.) (deforms at 120°). It was recrystallized twice from a mixture of anhydrous ethyl alcohol and acetone. It was a nearly colorless substance with a slight pistachio shade, rather readily soluble in water and acetone, insoluble in ether. M. p. 160° (decomp.) (deforms at 123.5° slightly); $[\alpha]^{18}D$ +10.65° (c 3.98; water).

Found %: C 57.19; H 6.68; N 3.71. $C_{37}H_{50}O_{16}N_2$. Calculated %: C 57.07; H 6.47; N 3.59.

The alcoholic mother liquor, after the separation of the crystalline precipitate, was evaporated in vacuo. There was left a residue of 40 mg (50%); m. p. 120° (decomp.). It was recrystallized twice from a mixture of anhydrous alcohol and acetone. In its appearance and properties it duplicates the previously described tartrate. M. p. 160° (decomp.) (deforms at 120°); $[\alpha]^{18}D$ +16.1° (c 1.88; water).

Found %: C 57.13; H 6.62. $C_{37}H_{50}O_{16}N_2$. Calculated %: C 57.07; H 6.47.

III. N-Acetyl-o-methylpsychotrine. 1) From o-methylpsychotrine prepared from quinolizine isolated after hydrogenation in the presence of platinum oxide in acid medium. a) N-Acetyl-o-methylpsychotrine base. The base of o-methylpsychotrine (0.55 g) was dissolved in 50 ml of ether and treated with 7.7 ml of 10% aqueous solution of potassium hydroxide and 0.8 ml of acetic anhydride. The mixture was shaken in a separatory funnel for 10 min. The aqueous layer was separated and the ethereal layer was washed with a potassium hydroxide solution. The extract was dried with potassium carbonate. After distillation of ether, there was isolated the base of N-acetyl-o-methylpsychotrine in the form of a colorless amorphous powder. The yield was 0.52 g (86%); m. p. 78-79° (deforms at 40°).

Found %: C 71.87; H 7.57; N 5.47. $C_{31}H_{40}O_5N_2$. Calculated %: C 71.49; H 7.75; N 5.38.

b) N-Acetyl-o-methylpsychotrine oxalate. This was prepared by treatment of an ethereal solution of the base with an ethereal solution of oxalic acid. The oxalate attracts atmospheric moisture during filtration. It was recrystallized twice from anhydrous methyl alcohol. It was a colorless substance, readily soluble in water, difficultly in alcohol and insoluble in ether. M. p. 148.5° (decomp.) (deforms at 142°). The melting point of a mixture of the oxalate of N-acetyl-o-methylpsychotrine with the oxalate of o-methylpsychotrine was 141.5-148° (decomp.) (deforms at 137°).

Found %: C 57.74; H 7.1. $C_{31}H_{40}O_5N_2 \cdot C_2H_2O_4 \cdot 4H_2O$. Calculated %: C 58.04; H 7.38.

2) From o-methylpsychotrine prepared from quinolizine isolated after hydrogenation in the presence of platinum oxide in neutral medium. a) N-Acetyl-o-methylpsychotrine base. This was prepared as indicated in the previous experiment in nearly quantitative yield. M. p. 98-99° (deforms at 97°).

Found %: C 71.75; H 7.50; N 51.3. $C_{31}H_{40}O_5N_2$. Calculated %: C 71.49; H 7.75; N 5.38.

b) N-Acetyl-o-methylpsychotrine oxalate, m. p. 152° (decomp.) (deforms at 146°). The melting point of a mixture of the oxalate of N-acetyl-o-methylpsychotrine with the oxalate of o-methylpsychotrine was 142-150° (decomp.) (deforms at 138°).

Found %: C 58.35; H 7.15. $C_{31}H_{40}O_5N_2 \cdot C_2H_2O_4 \cdot 4H_2O$. Calculated %: C 58.04; H 7.38.

3) From o-methylpsychotrine prepared from quinolizine isolated after hydrogenation in the presence of Raney nickel catalyst. a) N-Acetyl-o-methylpsychotrine base, m. p. 73-74° (deforms at 40°).

b) N-Acetyl-o-methylpsychotrine oxalate, m. p. 151° (decomp.) (deforms slightly at 143.5°). The melting point of a mixture of the oxalate of N-acetyl-o-methylpsychotrine and the corresponding oxalate of o-methylpsychotrine was 142.5-50° (deforms at 138.5°).

Found %: C 58.35; H 7.15. $C_{31}H_{40}O_5N_2 \cdot C_2H_2O_4 \cdot 4H_2O$. Calculated %: C 58.04; H 7.38.

SUMMARY

1. The synthesis of isomeric o-methylpsychotrines was accomplished.

2. The studies made on o-methylpsychotrine and its acyl derivatives permit us to conclude that the bases and the salts of the alkaloids have predominantly endocyclic N=C position of the double bond. In the alkaline medium there occurs a migration of hydrogen (prototropic rearrangement) with formation of an exocyclic C=C bond.

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FROM THE FIELD OF ORGANIC INSECTOFUNGICIDES

XXXIV. NEW METHOD OF SYNTHESIS OF TRIALKYL PHOSPHITES

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Various derivatives of phosphonic acids, such as, for example, the derivatives of phosphonoacetic acid, used for control of plant pests [1, 2] have received a practical application in agriculture as chemical means of protection of plants in recent years, along with the esters of phosphoric, thiophosphoric and dithiophosphoric acids. The basic raw material for the preparation of compounds of this type are the trialkyl phosphites which are beginning to acquire an independent significance in agriculture as the means for control of weeds [3]. In connection with this information we undertook a special study of the methods of preparation of trialkyl phosphites.

At the present time there have been described in the literature four methods of synthesis of trialkyl phosphites: 1) the method of A. E. Arbuzov, by the reaction of phosphorus trichloride with sodium alcoholates in ether or another suitable solvent [4, 5]; 2) the method of Milobendzki, by the reaction of phosphorus trichloride with alcohols in the presence of organic bases [6-8]; 3) the reaction of transesterification [14] and 4) from sodium salts of acid esters of carbonic acid and phosphorus trichloride [15]. Among the listed methods of preparation of trialkyl phosphites, the most practical interest, in our opinion, lies in the first two methods. However, in the second method one obtains a not very pure product, while in the first, one is obliged to work with metallic sodium which is inconvenient in some cases, while the yields at times do not rise over 20-30%.

Analogous to the method of preparation of esters of chlorothiophosphoric acid developed by us recently [16-18], we used for the preparation of trialkyl phosphites the reaction of phosphorus trichloride with magnesium alcoholates which are readily prepared from the corresponding alcohol and metallic magnesium.

$$2PCl_3 + (RO)_2Mg \rightarrow 2ROPCl_2 + MgCl_2$$
$$2ROPCl_2 + (RO)_2Mg \rightarrow 2(RO)_2PCl + MgCl_2$$
$$2(RO)_2PCl + (RO)_2Mg \rightarrow 2(RO)_3P + MgCl_2$$

As intermediate products there are formed the esters of chlorophosphorous acid, which under appropriate conditions may be isolated readily. The trialkyl phosphites may be obtained in 35-60% yields from this reaction. The compounds prepared by us and their properties are listed in the table.

EXPERIMENTAL

Preparation of trialkyl phosphites. As an example, we describe the preparation of triethyl phosphite by two methods.

1. To magnesium ethoxide prepared from 5.5 g of metallic magnesium (powder) and 27 ml of anhydrous ethyl alcohol in 75 ml of dry ether there was added over 30 min with good stirring 13.7 g of phosphorus trichloride. The temperature of the reaction mixture rose from 20° to the boiling point of ether during the addition of phosphorus trichloride. After addition of the entire amount of phosphorus trichloride, the reaction mixture was refluxed on a water bath for 1.5 hr. Then, after cooling, the precipitated magnesium chloride was filtered off, ether was distilled and the residue distilled in vacuo or at atmospheric pressure. B. p. 154-155°. Yield: 9-10 g (56-60%).

2. To dry powdered magnesium ethoxide suspended in 75 ml of absolute ether there was gradually added 13.7 g of phosphorus trichloride and the reaction mixture was worked up further as described above. Magnesium ethoxide was prepared by the dissolution of 5.5 g of metallic magnesium in 70 ml of anhydrous alcohol with a subsequent distillation of excess alcohol in vacuo from a water bath. The yield of triethyl phosphite by this method was 55%.

Under completely analogous conditions there were prepared the other trialkyl phosphites, except trimethyl phosphite, the yield of which was poor. It is possible to use benzene or petroleum ether as the solvent instead of ether, but the yields of trialkyl phosphites in these cases are lower.

Properties of Trialkyl Phosphites

Formula	Yield (in %)	d_4^{20}	n_D^{20}	B. p. (pressure in mm)	MR		P (in %)		C (in %)		H (in %)		Literature data [19, 20]		
					found	calc.	found	calc.	found	calc.	found	calc.	b. p. (pressure in mm)	d_4^{20}	n_D^{20}
$(C_2H_5O)_3P$	55—60	0.9665	1.4136	154—155°	42.75	42.97	18.50, 18.65	18,68	—	—	—		155—156° [19]	0.9777(0°)	1.4138
$(C_3H_7O)_3P$	41	0.9525	1.4290	83 (10)	56.41	56.82	14.58, 14.50	14.90	51.87, 52.06	51.90	10.17, 10.12	10.10	83 (10) [19]	0.9522	1.4265
$(C_4H_9O)_3P$	35	0.9267	1.4320	137 (26)	70.28	70.67	12.45, 12.51	12.40	57.41, 57.52	57.60	10.80, 10.81	10.80	127 (18) [20]	0.9253	1.4321
iso-$(C_4H_9O)_3P$	60	0.9060	1.4330	112 (14)	70.71	70.67	12.41, 12.46	12.40	57.30, 57.26	57.60	10.91, 10.86	10.80	135—136 (10) [19]	0.9036	—

SUMMARY

A new method of preparation of triaklyl phosphites in yields of 35-60% by the reaction of phosphorus trichloride with magnesium alcoholates has been developed and proposed.

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CATALYTIC SYNTHESIS OF KETONES

V. SYNTHESIS OF METHYL PHENYL, ETHYL PHENYL, METHYL n-PROPYL, AND DI-n-PROPYL KETONES

I. P. Iakovlev and D. P. Popa

One of us had previously made a supposition [1] that alcohols which cannot be dehydrated to ethylenic compounds should not form ketones and proposed a general scheme of ketonization [2]. In the present work the above supposition was verified experimentally and some theories were developed about the mechanism of ketonization in which two carbonyl-containing compounds take part in the reaction. We studied the following mixtures: 1) benzoic acid and ethyl alcohol, 2) acetic acid and benzyl alcohol, 3) benzoic acid and methyl alcohol, 4) benzaldehyde and acetic acid, 5) n-butyraldehyde, 6) n-butyraldehyde and acetic acid, and 7) ethyl benzoate and ethyl alcohol. Benzoic acid and methyl alcohol, and acetic acid and benzyl alcohol, as indicated earlier [1], should not form either acetophenone or methyl benzyl ketone, while benzoic acid and ethyl alcohol should yield ethyl phenyl ketone. The synthesis of methyl ethyl ketone from acetic acid and ethyl alcohol had been carried out earlier [3]. The reaction was run on chrome-manganese catalyst [8].

Actually, as shown by our experiments, neither acetophenone was formed from benzoic acid and methyl alcohol, nor was methyl benzyl ketone formed from acetic acid and benzyl alcohol, as expected, while ethyl phenyl ketone did form from benzoic acid and ethyl alcohol. It should be noted that in the reaction of acetic acid and benzyl alcohol there was observed the formation of acetophenone. This reaction does not fit either our schemes of ketonization reactions or the schemes according to which the formation of ketones proceeds either through esters or through aldols [4-7]. We supposed that the formation of acetophenone from acetic acid and benzyl alcohol proceeds analogously to the reaction of ketonization of acetic and benzoic acids. Benzyl alcohol is transformed by dehydrogenation at first into benzaldehyde, after which the resulting benzaldehyde reacts with acetic acid. This supposition is confirmed by the fact that in the reaction of acetic acid and benzaldehyde there is formed some acetophenone. This reaction showed that acetophenone is evidently formed in the reaction of acetic acid and benzaldehyde, but not benzyl alcohol, and that it is a special case of a general scheme of ketonization of compounds with carbonyl groups [2]. If this is correct, n-butyraldehyde should yield di-n-propyl ketone. The mixture of n-butyraldehyde and acetic acid should yield methyl propyl ketone, along with acetone and di-n-propyl ketone. Actually, during ketonization of a mixture of acetic acid with n-butyraldehyde there were obtained the expected ketones – acetone, methyl propyl ketone and di-n-propyl ketone.

The general scheme of ketonization of compounds which have carbonyl groups, proposed by us, permits one to forecast the direction of the ketonization processes. It would be possible, for example, to say that on the dehydrogenating catalysts, such as copper, there would be formed mainly acetone from a mixture of acetic acid and ethyl alcohol, while over a dehydrating catalyst, for example, aluminum oxide, methyl ethyl ketone would be formed.

EXPERIMENTAL

1. Experiments with benzoic acid and ethyl alcohol. A solution of ethanol saturated at room temperature with benzoic acid was fed from an automatic burette into the catalyst tube made of Pyrex glass, the feed rate being 15 ml per hour. The chrome-manganese catalyst [8] was deposited on asbestos wool.

For determination of optimum reaction conditions, the reaction was run at 440, 450 and 460°. In all experiments hydrogen was supplied to the system at the rate of 75 ml per min. The hydrogen was obtained from arsenic-

Composition of the starting mixture	Amount (ml)		B. p. and amount of main fraction (in g)	Low boiling fraction and its amount (in g)	Melting point			Name of ketone	Yield of ketone (in %)	Constants of main fraction				Remarks
	of mixture run through	of catalyzate			of 2,4-dinitrophenylhydrazone of ketone of main fraction	of 2,4-dinitrophenylhydrazone of ketone, [9]	of semicarbazone of ketone of main fraction			d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	
Benzoic acid + ethyl alcohol [a]	150	58	215—220° (2.6)	170—215° (4.8)	189—192°	191°	178°	Ethyl phenyl ketone	7[c]	1.020	1.525	40.32	40.17	Fraction with b. p. 170-215° consisted mainly of benzaldehyde
Ethyl benzoate + + ethyl alcohol (0.28 : 2) [b]	147	28	216—223 (3.7)	200—208 (6.6)	190—192	191		Ethyl phenyl ketone	7.8[e]	—	—	—	—	Experiment was run with H_2 gas
Benzyl alcohol + + acetic acid (1 : 1) [b]	65	53	190—202 (2.0)		242—243	249	197	Acetophenone		—	—	—	—	Experiments were run with H_2 and without H_2. Besides acetophenone, there were isolated: acetone, toluene, benzaldehyde
Benzaldehyde + + acetic acid (1 : 4) [b]	55	44	196—205 (2.1)	189—196 (0.7)	240—242	249	197—198	Acetophenone	13[d]	1.030	1.538	36.44	35.55	Feed rate 12 ml per hr
Benzoic acid + + methyl alcohol [a]	50	36	176—187 (11.5)		236	237	226	Benzaldehyde		1.045	1.540	31.86	30.93	Experiments were run with H_2 and without it
n-Butyraldehyde	55	21.5	142—148 (9.1)		73—74	75		Di-n-propyl ketone	41	0.821	1.406	34.16	34.53	Experiments were run with H_2 at 440°
Acetic acid + n-butyraldehyde (4.5 : 1) [b]	190	91	140—148 (6.6)		74	75		Di-n-propyl ketone	35.5[d]	0.8213	1.406	34.00	34.53	Experiments were run without H_2
			99—105 (8.1)		142	143		Methyl-n-propyl ketone	28.8[d]	0.8095	1.388	25.20	26.11	

a) Saturated solution at room temperature; b) molar ratio; c) calculated on the acid; d) calculated on the aldehyde; e) calculated on the ester.

free zinc and dilute sulfuric acid. The catalyzate, after being dried, was subjected to fractional distillation. The results of this and subsequent experiments are shown in the table. The optimum reaction temperature was found to be 450° and the experiments were run at this level.

Fractions with b. p. 170-251° consisted mainly of benzaldehyde and a small amount of acetophenone. A few drops of the fraction were taken at the beginning and the end of distillation for preparation of derivatives with 2,4-dinitrophenylhydrazine. The tests of the resulting 2,4-dinitrophenylhydrazones of acetone and benzaldehyde in mixed melting points with authentic compounds gave respective m. p. 234° and 243°. The fraction with b. p. 215-220° was ethyl phenyl ketone (b. p. 218°). Ethyl phenyl ketone was characterized by the melting points of its 2,4-dinitrophenylhydrazone and semicarbazone.

2. Experiments with ethyl benzoate and ethyl alcohol were run at 450° over chrome-manganese catalyst (15 g) deposited on asbestos wool. The feed rate of the initial mixture was 50 ml/hr; hydrogen was supplied at the rate of 100 ml/min. Two layers formed – aqueous and oily. The latter was separated and dried over sodium sulfate. After distillation there were isolated: acetone, acetophenone and ethyl phenyl ketone. The yield of ethyl phenyl ketone, as in the previous experiment, was negligible.

3. Experiments with benzyl alcohol and acetic acid, were run under conditions analogous to those described for the 1st experiment. Acetophenone was characterized by the melting point of its derivatives, whose mixed melting points gave no depression. It was impossible to fractionate the mixture into the various components in this experiment. As follows from our scheme, evolution of carbon monoxide should occur in the formation of acetophenone from acetic acid and benzyl alcohol. Actually, the gas analysis run in the VTI apparatus confirmed our expectations. In the off-gases there were found 38% of carbon monoxide and 1.5% carbon dioxide; unsaturated hydrocarbons were absent, while hydrogen was not determined.

4. Experiments with benzaldehyde and acetic acid. For confirmation of the fact that acetophenone is formed from benzyl alcohol and acetic acid through benzaldehyde, there was run an experiment with these substances. The results were similar to those from the preceding experiment (see Table).

5. Experiments with methyl alcohol and benzoic acid were run analogously with those described in Expt. 1. Methanol and benzaldehyde were detected in the examination of the resulting catalyzate. No acetophenone was found.

6. Experiments with n-butyraldehyde and its mixture with acetic acid were run under conditions analogous to those described in Expt. 1.

SUMMARY

The reaction of ketonization of acids and aldehydes over a chrome-manganese catalyst was studied. From a mixture of acetic acid and benzyl alcohol it was impossible to isolate any methyl benzyl ketone. No acetophenone was formed from benzoic acid and methanol. Benzoic acid and ethyl benzoate form ethyl phenyl ketone with ethanol. n-Butyraldehyde with acetic acid gave methyl n-propyl ketone and di-n-propyl ketone. Benzaldehyde and acetic acid gave acetophenone.

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REACTION OF PHOSPHORUS PENTACHLORIDE WITH AMIDES OF PHOSPHORIC ACID

A. V. Kirsanov and I. N. Zhmurova

In the reaction of phosphorus pentachloride with aryl- and alkylsulfonamides [1], amides of carboxylic acids [2] and amides of carbonic acid [3] there are formed the corresponding trichlorophosphazo compounds. This allows one to suppose that this reaction has a general character and could be extended to amides of other acids, including phosphoric and thiophosphoric. In reality, diphenyl phosphoramidate and diphenyl thiophosphoramidate react with phosphorus pentachloride yielding thereby the diphenyl esters of trichlorophosphazophosphoric and trichlorophosphazothionophosphoric acids.

$$(C_6H_5O)_2PONH_2 + PCl_5 \longrightarrow 2HCl + \underset{(I)}{(C_6H_5O)_2PON{=}PCl_3}$$

$$(C_6H_5O)_2PSNH_2 + PCl_5 \longrightarrow 2HCl + \underset{(II)}{(C_6H_5O)_2PSN{=}PCl_3}$$

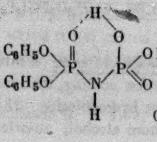
The reaction proceeds in almost quantitative yield at room temperature.

Trichlorophosphazo compounds (I) and (II) are colorless viscous liquids which are readily soluble in benzene, carbon tetrachloride and dioxane, insoluble in petroleum ether. They are slowly hydrolyzed by water and atmospheric moisture.

Diphenyl ester of trichlorophosphazophosphoric acid forms the diphenyl ester of trianilinophosphazophosphoric acid, $(C_6H_5O)_2PON{=}P(NHC_6H_5)_3$, on being heated with aniline in a benzene solution. The diphenyl ester of trichlorophosphazothionophosphoric acid forms, in its reaction with aniline, a viscous extensible mass from which we failed to isolate any individual substances.

In the hydrolysis of substances (I) and (II) with formic acid there are formed the corresponding dichlorides: $(C_6H_5O)_2PONHPOCl_2$ (III) and $(C_6H_5O)_2PSNHPOCl_2$ (IV). The dichloride (III) is a viscous liquid which is soluble in benzene, carbon tetrachloride and dioxane, insoluble in petroleum ether. The dichloride (IV) is a colorless crystalline substance, readily soluble in dioxane, less soluble in benzene and carbon tetrachloride and insoluble in petroleum ether. Dichlorides (III) and (IV) react with aniline, yielding, respectively, the P,P-dianilide of P',P'-diphenyl ester of imidodiphosphoric acid and P,P-dianilide of P',P'-diphenyl ester of P'-thionoimidodiphosphoric acid: $(C_6H_5O)_2PONHPO(NHC_6H_5)_2$ and $(C_6H_5O)_2PSNHPO(NHC_6H_5)_2$: colorless crystalline substances which have acidic character. They are titrated by one equivalent of alkali in an alcoholic solution.

In the reaction of diphenyl ester of trichlorophosphazophosphoric acid (I) with water there is formed, in good yield, the P,P-diphenyl ester of imidodiphosphoric acid, $(C_6H_5O)_2PONHPO(OH)_2$ (V). The hydrolysis with hot water requires a few minutes, while at room temperature the reaction is completed in 1 day. Substance (V) forms colorless crystals soluble in alcohol and dioxane, very difficultly soluble in water, and insoluble in benzene, ether or petroleum ether. The extraordinary stability of the N—P bond in substance (V) attracts attention. The aryl- and alkylsulfonamidophosphoric and acylamidophosphoric acids, analogous to it, are hydrolyzed comparatively readily by water yielding the corresponding amides [4], while the diphenyl ester of imidodiphosphoric acid is not decomposed by being boiled with water for 5-10 min. Aryl- and alkylsulfonamidophosphoric acids and acylamidophosphoric acids are readily soluble in cold water [4], but substance (V) is very difficultly soluble in water. Such unusual properties of the P,P-diphenyl ester of imidodiphosphoric acid are caused, in all probability, by the presence of an intramolecular hydrogen bond:


(V)

As is known, the sulfur atom is not inclined to form a hydrogen bond. Therefore, the diphenyl ester of trichlorophosphazothionophosphoric acid (II) is slowly decomposed in its reaction with water, yielding diphenyl thionophosphoramidate and phosphoric acid, without forming a sulfur analog of (V).

Diphenyl esters of trichlorophosphazophosphoric (I) and thionophosphoric (II) acids yield, in reactions with sodium aryloxides, the triaryloxy phosphazo compounds of types: $(C_6H_5O)_2PON{=}P(OR)_3$ (VI) and $(C_6H_5O)_2PSN{=}P(OR)_3$ (VII), which form colorless crystalline substances of neutral character.

Dichlorides (III) and (IV) react with alcoholates and phenolates forming tetra esters of the types: $(C_6H_5O)_2 \cdot PONHPO(OR)_2$ (VIII) and $(C_6H_5O)_2PSNHPO(OR)_2$ (IX). Tetraphenyl esters of types (VIII) and (IX) were also prepared by hydrolysis of diphenyl esters of triphenoxyphosphazophosphoric acids of types (VI) and (VII) according to the scheme:

$$(C_6H_5O)_2PON{=}P(OC_6H_5)_3 \xrightarrow{+2NaOH} C_6H_5ONa + H_2O + (C_6H_5O)_2PONNaPO(OC_6H_5)_2$$

For running this reaction it is unnecessary to isolate the appropriate triphenoxy phosphazo compound in the pure form and one may start directly with the crude reaction products of diphenyl esters of trichlorophosphazophosphoric and trichlorophosphazothionophosphoric acids with sodium phenoxide (see experimental section).

Di-p-nitrotetraphenyl esters of types (VIII) and (IX) are subject to a very rapid further hydrolysis on being heated with alkali. Therefore, in the hydrolysis of diphenyl ester of tri-p-nitrophenoxyphosphazophosphoric acid (VI, R = $C_6H_4NO_2$-p) with caustic alkali it is impossible to isolate the corresponding dinitrotetraphenyl ester, while after a brief heating with alkali of the diphenyl ester of tri-p-nitrophenoxyphosphazothionophosphoric acid (VII, R = $C_6H_4NO_2$-p) it was possible to isolate the dinitrotetraphenyl ester in a yield of but 12%. The diphenyl esters of triaryloxyphosphazophosphoric acids are not hydrolyzed by solutions of caustic alkalies at room temperature or by soda solutions at the boiling point.

P,P-Di-p-nitrotetraphenyl ester of P'-thionoimidodiphosphoric acid was prepared in 22% yield from the P,P-dichloride of P',P'-diphenyl ester of P'-thionoimidodiphosphoric acid (IV) and sodium p-nitrophenoxide. From the P,P-dichloride of P',P'-diphenyl ester of imidodiphosphoric acid (III) and sodium p-nitrophenoxide we could not prepare the corresponding tetra ester.

Tetraaryl esters of imidodiphosphoric and thionoimidodiphosphoric acids of types (VIII) and (IX) are colorless crystalline compounds with acid character. They are titrated by one equivalent of alkali in an alcoholic solution.

EXPERIMENTAL

Diphenyl ester of trichlorophosphazophosphoric acid (I). A mixture of 0.1 mole of diphenyl phosphoramidate and 0.1 mole of phosphorus pentachloride was allowed to stand at room temperature. Evolution of hydrogen chloride began soon and the mixture liquefied gradually. After 5-6 hrs the reaction mixture was heated for 30 min to 50-60°. The resulting diphenyl ester of trichlorophosphazophosphoric acid was a colorless viscous liquid; yield: 99.4%.

Found %: Cl 27.70. Equivalents after hydrolysis 4.97. $C_{12}H_{10}O_3NCl_3P_2$. Calculated %: Cl 27.78. Equivalents after hydrolysis 5.00.

Diphenyl ester of trichlorophosphazothionophosphoric acid (II) was prepared analogously to the preceding compound. It was a colorless viscous liquid; yield: 99.5%.

Found: equivalents after hydrolysis 4.86. $C_{12}H_{10}O_2NCl_3P_2S$. Calculated: equivalents after hydrolysis 5.00.

Diphenyl ester of trianilinophosphazophosphoric acid. A mixture of 0.01 mole of (I), 10 ml of benzene and 0.06 mole of aniline was refluxed for 5 hrs. After cooling, the resulting precipitate was filtered off and washed with benzene and with water to remove aniline hydrochloride. The water-insoluble diphenyl ester of trianilinophosphazophosphoric acid was recrystallized from alcohol; colorless plates; yield: 76%; m. p. 195-197°.

Found %: N 10.33. $C_{30}H_{28}O_3N_4P_2$. Calculated %: N 10.01.

P,P-Dichloride of P',P'-diphenyl ester of imidodiphosphoric acid (III). A mixture of 0.1 mole of (I) and 0.1 mole of anhydrous formic acid was heated to 90-100°, then to 120-125° until gas evolution ceased (about 1.5-2 hrs). The resulting dichloride was a colorless, very viscous liquid; yield: 99.5%.

Found: equivalents after hydrolysis 3.91. $C_{12}H_{11}O_4NCl_2P_2$. Calculated: equivalents after hydrolysis 4.00.

P,P-Dichloride of P',P'-diphenyl ester of P'-thionoimidodiphosphoric acid (IV). A mixture of 0.1 mole of (II), 0.1 mole of anhydrous formic acid and 10 ml of dry benzene was heated to 30-35° for 3 days until the gas bubbles ceased to be formed. 20 ml of petroleum ether was added to the reaction mixture and the resulting precipitate was filtered off and recrystallized from carbon tetrachloride. Yield: 30%. Colorless needles with m. p. 102-104°.

Found %: Cl 18.73. Equivalents after hydrolysis 4.06. $C_{12}H_{11}O_3NCl_2SP_2$. Calculated %: Cl 18.64. Equivalents after hydrolysis 4.00.

P,P-Dianilide of P',P'-diphenyl ester of imidodiphosphoric acid. A mixture of 0.01 mole of (III), 10 ml of benzene and 0.04 mole of aniline was refluxed for 5 hrs. The resulting precipitate was filtered off and washed with benzene, then with water to remove aniline hydrochloride. The water-insoluble dianilide was recrystallized from methanol. Colorless needles; yield: 54%; m. p. 197-198°.

Found %: N 9.02. Equivalents 1.00. $C_{24}H_{23}O_4N_3P_2$. Calculated %: N 8.77. Equivalents 1.00.

P,P-Dianilide of P',P'-diphenyl ester of P'-thionoimidodiphosphoric acid was prepared from substance (IV) analogously to the preceding one; yield 98%; m. p. 198-200° (from alcohol).

Found %: N 8.68. $C_{24}H_{23}O_3N_3P_2S$. Calculated %: N 8.48.

P,P-Diphenyl ester of imidodiphosphoric acid (V). To 0.01 mole of (I) there was added 5 ml of water and the mixture was left overnight. The precipitated crystals of (V) were filtered off, washed with water, dried in air, dissolved in dioxane and precipitated with ether. It formed a colorless crystalline powder; m. p. 170-172°; yield: 83%.

Found %: N 4.43. Equivalents 2.09. M (in dioxane) 340, 348. $C_{12}H_{13}O_6NP_2$. Calculated %: N 4.25. Equivalents 2.00. M 329.

Diphenyl ester of triphenoxyphosphazophosphoric acid (VI, R = C_6H_5). To a solution of 0.02 mole of (I) in 25 ml of benzene there was added in one portion with energetic stirring 0.06 mole of sodium phenoxide. The mixture warmed up rather considerably owing to the heat of reaction and the sodium phenoxide passed into solution while a slimy precipitate of sodium chloride formed. After the heat evolution had ceased, the mixture was refluxed for 1 hr. After cooling, the sodium chloride was washed off with water, the benzene layer was separated, benzene was removed from it on a water bath and the residual oil was triturated with water until it crystallized. The crystalline product was filtered off, dried in air and recrystallized from a mixture of benzene and petroleum ether. Yield: 76% needles with m. p. 72-74°.

Found %: N 2.56. $C_{30}H_{25}O_6NP_2$. Calculated %: N 2.51.

Diphenyl ester of triphenoxyphosphazothionophosphoric acid (VII, R = C_6H_5) was prepared analogously to the preceding one. The crude specimen was washed with methanol and recrystallized from methanol. Prisms with m. p. 96-98°. Yield: 69%.

Found %: N 2.62. $C_{30}H_{25}O_5NSP_2$. Calculated %: N 2.44.

Diphenyl ester of tri-p-nitrophenoxyphosphazophosphoric acid (VI, R = $C_6H_4NO_2$-p). A mixture of 0.01 mole of (I), 0.03 moles of anhydrous sodium p-nitrophenoxide and 15 ml of dioxane was refluxed until the nitrophenoxide color faded out (about 2 hrs), after which it was poured into water. The resulting oil crystallized rapidly and the crystals were filtered off, washed with methanol and recrystallized from benzene. Yield: 78%. M. p. 132-134°.

Found %: N 8.30. $C_{30}H_{22}O_{12}N_4P_2$. Calculated %: N 8.09.

Diphenyl ester of tri-p-nitrophenoxyphosphazothionophosphoric acid (VII, R = $C_6H_4NO_2$-p) was prepared analogously to the preceding compound. Yield: 70%. M. p. 154-156°; prisms from benzene.

Found %: N 7.90. $C_{30}H_{22}O_{11}N_4SP_2$. Calculated %; N 7.90.

Diphenyl ester of tri-p-chlorophenoxyphosphazothionophosphoric acid (VII, R = C_6H_4Cl-p). 0.06 g-mole of p-chlorophenol was added to a solution of sodium methoxide prepared from 0.06 g-atom of sodium and 20 ml of methanol. The methanol was distilled in vacuo and to the solid phenoxide was added 25 ml of benzene and 0.02 mole of (I). The mixture was heated to boiling for 1.5 hrs, the precipitated sodium chloride was washed away with water, the benzene layer was separated, the benzene was distilled from it and the residual oil was triturated with methanol, after which it crystallized. The crystals were filtered off and recrystallized from methanol. Prisms with m. p. 69-71°. Yield: 36%.

Found %: Cl 15.79. $C_{30}H_{22}O_5NCl_3P_2$. Calculated %: Cl 15.74.

P,P-Dimethyl P',P'-diphenyl ester of imidodiphosphoric acid (VIII, R = CH_3). A solution of 0.06 mole of sodium methoxide in 20 ml of methanol was slowly added with stirring and cooling with ice water to a solution of 0.02 mole of (III) in 25 ml of benzene. The solvents were distilled off in vacuo on a water bath and the sirupy residue (a mixture of sodium chloride and the sodium salt of the tetra ester) was dissolved in 10 ml of water. The solution was acidified with hydrochloric acid and the precipitated oil (free tetra ester) was extracted with chloroform; chloroform was distilled off, the oily residue was dissolved in methanol, the solution was boiled with activated charcoal, filtered and the methanol was distilled off in vacuo. The residue was the tetra ester in the form of a viscous slightly yellowish oil; yield: 90%.

Found %: N 3.90. Equivalents 1.00. $C_{14}H_{17}O_6NP_2$. Calculated %: N 3.90. Equivalents 1.00.

P,P-Diethyl P',P'-diphenyl ester of imidodiphosphoric acid (VIII = C_6H_5) was prepared just like the preceding compound but, after the acidification of the aqueous solution of the salt, the free tetra ester was extracted with ether. The further work-up was as above. The tetra ester was a slightly yellowish viscous oil. Yield: 93%.

Found %: N 3.63. Equivalents 1.00. $C_{16}H_{21}O_6NP_2$. Calculated %: N 3.64. Equivalents 1.00.

Tetraphenyl ester of imidodiphosphoric acid (VIII, R = C_6H_5). A. From P,P-dichloride of P',P'-diphenyl ester of imidodiphosphoric acid. To a mixture of 0.06 mole of sodium phenoxide and 25 ml of benzene there was added, with energetic stirring, a solution of 0.02 mole (III) in 10 ml of benzene. After the vigorous reaction had been completed, the mixture was refluxed for 1 hr, after which benzene was distilled off in vacuo; the residue was treated with 25 ml of water and with enough hydrochloric acid to give an acid test with Congo red. The precipitated oil was separated from the aqueous layer by decantation and was rubbed with 50% methanol. The resulting crystalline precipitate was filtered off and recrystallized from a mixture of benzene and petroleum ether. Yield: 13%. Needles, m. p. 110-112°.

Found %: N 3.11. Equivalents 1.01. $C_{24}H_{21}O_6NP_2$. Calculated %: N 2.91. Equivalents 1.00.

B) From diphenyl ester of trichlorophosphazophosphoric acid. A solution of 0.02 mole of (I) in 10 ml of benzene was added to a suspension of sodium phenoxide in 25 ml of benzene. The reaction proceeded with heat evolution. After the heat evolution had ceased, the mixture was refluxed for 1 hr, after which it was washed with water, the benzene layer was separated and the benzene was distilled in vacuo. To the residue there was added 20 ml of methanol and 20 ml of N solution of sodium hydroxide. The mixture was refluxed for 30 min, poured into water and acidified. The tetraphenyl ester of imidodiphosphoric acid, which precipitated as an oil, crystallized rapidly. The crystals were filtered off, treated with a small volume of methanol to remove the colored impurities and recrystallized from a mixture of benzene and petroleum ether. Yield: 57%. The tetra ester melted at 110-112° and gave no depression in mixed melting point with the substance prepared in the preceding experiment.

P,P-Dimethyl P',P'-diphenyl ester of P'-thionoimidodiphosphoric acid (IX, R = CH_3). To a mixture of 0.02 mole of (IV) and 20 ml of benzene there was added, with ice water cooling and energetic stirring, a solution of 0.06 mole of sodium methoxide in 20 ml of methanol, the addition being made gradually. The solvents were distilled in vacuo, the residual thick sirup was dissolved in water and the solution was acidified. An oil precipitated and soon crystallized. The crystals were filtered off and recrystallized from a mixture of benzene and petroleum ether. Prisms with m. p. 115-117°. Yield: 90%.

Found %: N 3.84. Equivalents 1.00. $C_{14}H_{17}O_5NSP_2$. Calculated %: N 3.72. Equivalents 1.00.

P,P-Diethyl P',P'-diphenyl ester of P'-thionoimidodiphosphoric acid (IX, R = C_2H_5) was prepared analogously to the preceding compound. Yield: 81%. M. p. 67-69° (from a mixture of carbon tetrachloride and petroleum ether).

Found %: N 3.38. Equivalents 1.01. $C_{16}H_{21}O_5NSP_2$. Calculated %: N 3.49. Equivalents 1.00.

Tetraphenyl ester of thionoimidodiphosphoric acid (IX, R = C_6H_5). A. From P,P-dichloride of P',P'-diphenyl ester of P'-thionoimidodiphosphoric acid. The tetra ester was prepared analogously to the tetraphenyl ester of imidodiphosphoric acid (method A). Yield: 87%. M. p. 100-102° (from a mixture of benzene and petroleum ether).

Found %: N 3.02. Equivalents 1.00. $C_{24}H_{21}O_5NSP_2$. Calculated %: N 2.82. Equivalents 1.00.

B. From diphenyl ester of trichlorophosphazothionophosphoric acid. The tetra ester was prepared analogously to the tetraphenyl ester of imidodiphosphoric acid (method B). Yield: 53%. M. p. 100-102° (from a mixture of benzene and petroleum ether). The product did not give a depression in mixed melting point with the substance prepared by method A.

P,P-Diphenyl P',P'-di-p-chlorophenyl ester of P-thionoimidodiphosphoric acid (IX, R = p-ClC_6H_4). To a solution of 0.03 mole of sodium methoxide in 20 ml of methanol there was added 0.03 mole of p-chlorophenol, the methanol was distilled in vacuo and to the dry sodium p-chlorophenoxide there was added the solution of 0.01 mole of (II) in 20 ml of benzene. The mixture was refluxed for 2 hrs, washed with water, the benzene layer was separated and benzene was distilled in vacuo. To the residue there was added 20 ml of N solution of sodium hydroxide in methanol. The mixture was refluxed for 1 hr, poured into water and acidified. The separated oil was removed from water by decantation and was treated with a small volume of methanol, after which it crystallized. The crystals were filtered off and recrystallized from alcohol. Needles, m. p. 144-146°. Yield: 34%.

Found %: Cl 12.45. Equivalents 1.00. $C_{24}H_{19}O_5NCl_2P_2S$. Calculated %: Cl 12.54. Equivalents 1.00.

P,P-Di-p-nitrotetraphenyl ester of P'-thionoimidodiphosphoric acid (IX, R = $C_6H_4NO_2$-p). A. From diphenyl ester of tri-p-nitrophenoxyphosphazothionophosphoric acid. A mixture of 0.02 mole of the ester and 20 ml of 2 N solution of sodium hydroxide in methanol was refluxed for 10 min. The resulting yellow homogeneous solution was poured into water and acidified. The resulting oil was separated from water by decantation and was triturated with methanol. The crystalline precipitate was filtered off and recrystallized from alcohol. Yield: 12%. M. p. 174-76°.

Found %: N 7.12. $C_{24}H_{19}O_9N_3SP_2$. Calculated %: N 7.15.

B. From P,P-dichloride of P',P'-diphenyl ester of P'-thionoimidodiphosphoric acid. A mixture of 0.01 mole mole of (IV), 15 ml of dioxane and 0.03 mole of anhydrous sodium p-nitrophenoxide was refluxed until the p-nitrophenoxide had disappeared, after which it was poured into water and acidified. The resulting oil was separated from water by decantation and was treated with a small volume of methanol. The resulting crystalline precipitate was washed and recrystallized from alcohol. The purified product melted at 174-176° and did not give a depression in mixed melting point with the substance prepared by method A.

SUMMARY

1. It was shown that diphenyl phosphoramidate and diphenyl thionophosphoramidate react with phosphorus pentachloride, forming trichlorophosphazo compounds thereby.

2. The hydrolysis of the trichlorophosphazo compounds, their reactions with aniline, alcoholates and phenoxides were studied.

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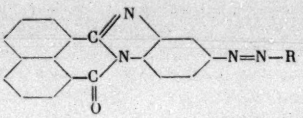
DIRECT AZO DYES – DERIVATIVES OF 1,8-NAPHTHOYLENE-1',2'-BENZIMIDAZOLE

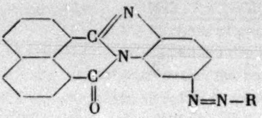
B. M. Krasovitskii, R. M. Matskevich, N. A. Radochina,

and K. P. Riazanova

The positive effect which is directed to the substantivity of dyes by the presence of the imidazole ring in their molecules had been noted a long time ago [1-3]. In continuation of these studies, B. A. Porai-Koshits and Ch. Frankovskii recently prepared some disazo dyes – derivatives of benzimidazole, which are well fixed by the cotton fiber [4]. Some years ago we had prepared some monoazo dyes from 1,8-naphthoylene-4'-amino-1',2'-benzimidazole (I) and 1,8-naphthoylene-5'-amino-1',2'-benzimidazole (II); these azo dyes were tested as acid dyes [5].



(I)

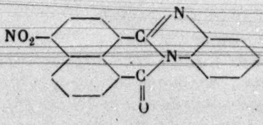


(II)

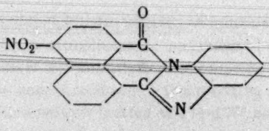
(R – azo component)

The goal of the present study is the synthesis of monoazo dyes which are isomeric with the previously prepared dyes (I) and (II), with the azo group being in the naphthalene nucleus of the structure of naphthoylenebenzimidazole, and of disazo dyes which contain azo groups both in the benzene and the naphthalene nuclei of this structure.

We used 4-nitronaphthalic anhydride, as the starting material for the preparation of the monoazo dyes; the substance was converted, by condensation with o-phenylenediamine, into the corresponding nitro derivative of 1,8-naphthoylene-1',2'-benzimidazole; the latter was reduced to the amine, which then served as the azo component for the azo dyes. In the reaction of 4-nitronaphthalic anhydride with o-phenylenediamine there is possible the formation of two isomeric products (III) and (IV).

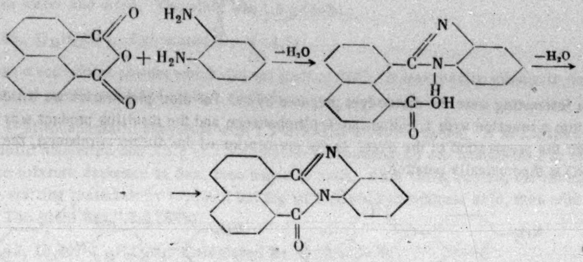


(III)

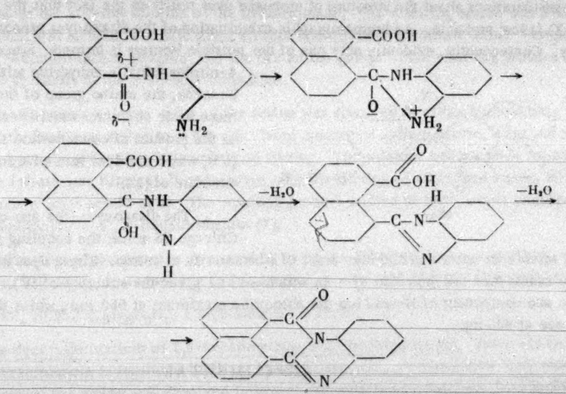


(IV)

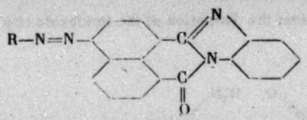
A chromatographic examination of the monoazo dyes prepared by us showed their homogeneity, which fact evidently testifies that the reaction of 4-nitronaphthalic anhydride with o-phenylenediamine yields but one product. The studies carried out by us at an earlier date [5, 6] permitted us to express some considerations about the mechanism of the process of formation of 1,8-naphthoylene-1',2'-benzimidazole from naphthalic anhydride and aromatic o-diamines [6]. Our experimental data agree very well with the supposition that during the reaction of naphthalic anhydride with o-diamines the formation of the imidazole ring takes place before that of the imide ring.



On the basis of studies [7] it is possible to consider that in the first stage of this process there is formed the monoacyl derivative of the o-diamine. Then, commencing with the suppositions developed by B. A. Porai-Koshits [8], it is possible to suppose that this monoacyl derivative suffers the following changes: as the result of intrusion of the unshared electron pair of nitrogen of the amino group into the electron deficiency at the carbon atom of the carbonyl group, there is formed the addition product which after an intramolecular rearrangement and loss of a molecule of water is transformed into the derivative of naphthalenemonocarboxylic acid containing the imidazole ring; this substance, in turn, by losing a molecule of water is transformed into 1,8-naphthoylene-1',2'-benzimidazole.

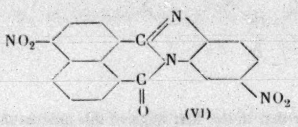


By using this scheme for the consideration of the reaction between 4-nitronaphthalic anhydride and o-phenylenediamine, we may make a supposition about the structure of the product that is formed thereby. In the molecule of 4-nitronaphthalic anhydride one of the carbonyl groups is bound with the nitro group by a shorter chain of conjugated double bonds than the other carbonyl group. Electronic deficiency at the carbon atom of this carbonyl group should be greater, owing to the electron-acceptor action of the nitro group, than that at the carbon atom of the other carbonyl; therefore, one may expect the formation of a nitro product having the structure (III). In this case, the dyes formed from this nitro compound should have the structure (V). These monoazo dyes have considerable substantivity to cotton, but are relatively poorly soluble in water and yield uneven color on the cloth.

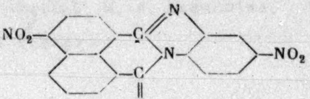


(V)

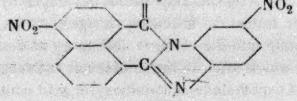
More interesting were the disazodyes prepared by us. For their preparation we introduced 4-nitronaphthalic anhydride into a reaction with 1,2-diamino-4-nitrobenzene and the resulting product was reduced to the diamine necessary for the preparation of the dyes. In the preparation of the dinitro compound, the formation of four isomers (VI-IX) is theoretically possible.



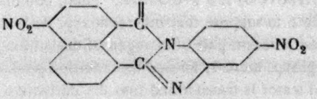
(VI)



(VII)

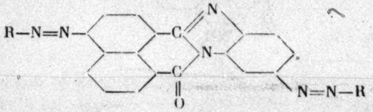


(VIII)



(IX)

The above considerations about the structure of monoazo dyes testify to the fact that the formation of isomers (VIII) and (IX) is less probable. A chromatographic examination of the disazo dyes prepared by us showed their homogeneity. Consequently, evidently only one of the possible isomers is formed. Since, in the reaction of 4-nitronaphthalic anhydride with 1,2-diamino-4-nitrobenzene, the amino group of the diamine which has the more basic character should react first, one may assign to the product of condensation the structure shown as (VI), while the dyes formed from it may be given the structure of (X).



(X)

The disazo dyes (the azo components were H- and Chicago SS acids; the coupling was run in basic medium) were readily soluble in water and had high order of substantivity to cotton. These dyes have deeper pigmentation in aqueous solutions than the monoazo dyes for which we had given the structure of (V). Thus, for example, disazo dyes with the azo component of H-acid has the absorption maximum at 560 mμ, while the corresponding monoazo dye has one at 600 mμ.

EXPERIMENTAL

4(5?)-Nitro-1,8-naphthoylene-1',2'-benzimidazole. A mixture of 4-nitronaphthalic anhydride (5 g) and o-phenylenediamine (3 g) was suspended in glacial acetic acid and heated at reflux on a sand bath. During the first 10 min of refluxing there precipitated a dense yellow precipitate, which failed to change after 3 hrs of heating. The resulting precipitate was filtered off and boiled with dilute hydrochloric acid, followed by water, 5% solution of sodium carbonate and again water, for freeing it from admixtures of the starting materials. The yield was 4.4 g (69%).

Found %: N 13.42, 13.28. $C_{18}H_9O_3N_3$. Calculated %: N 13.33.

The resulting substance was a yellow powder which did not have a sharp melting point but which shrank and darkened at 250-257°; it was soluble in the cold in concentrated sulfuric acid, and in hot benzene and methyl alcohol.

4(5?)-Amino-1,8-naphthoylene-1',2'-benzimidazole. 4 g of the nitro compound was suspended in 25 ml of pyridine, heated to boiling, and treated dropwise with 25 ml of N solution of sodium polysulfide in pyridine, the mixture being heated for 15 min and then poured into water; a red-violet precipitate formed, which was filtered off, washed with water and dried. The yield was 1.8 g (50%).

Found %: N 14.40. $C_{18}H_{11}ON_3$. Calculated %: N 14.74.

The substance was a red-violet powder which did not melt at 300°; it was readily soluble in cold concentrated sulfuric acid, glacial acetic acid and methyl alcohol.

Condensation of 4-nitronaphthalic anhydride with 1,2-diamino-4-nitrobenzene. A well triturated mixture of 6 g of 4-nitronaphthalic anhydride and 3.6 g of 1,2-diamine-4-nitrobenzene was heated for 1 hr on an oil bath, preheated to 185°. The mixture darkened at first, then began to melt. After being cooled, the reaction product was washed free of the starting materials by repeated boiling with dilute hydrochloric acid, then with 5% solution of sodium carbonate. The yield was 7.8 g (88%).

Found %: N 15.43, 15.46. $C_{18}H_8O_5N_4$. Calculated %: N 15.55.

The product was a yellow powder with m. p. 261° (after reprecipitation with water from a pyridine solution), which was readily soluble in pyridine and in hot methyl alcohol and glacial acetic acid.

Reduction of dinitro compound. 2 g of the dinitro compound in 40 ml of methyl alcohol was heated on a water bath to boiling under a reflux condenser, treated with 20 ml of water and under continued refluxing was gradually treated with 10 g of sodium hydrosulfite. The nitro compound went into solution during the addition of the hydrosulfite and the solution gradually changed its color from yellow to dark red. After the addition of the entire amount of the hydrosulfite, the refluxing was continued for 1 hr longer, after which the solution was filtered and the filtrate was evaporated nearly to dryness. After addition of concentrated hydrochloric acid there formed a precipitate of bright red crystals of the hydrochloride of the amine. The free base was liberated by the addition of ammonium hydroxide to the aqueous solution of the hydrochloride. The resulting amine was a dark brown powder with m. p. 360°, which was soluble in acetic acid, alcohol and dilute hydrochloric acid. The presence of the 1,8-naphthoylene-1',2'-benzimidazole grouping and the two amino groups in the resulting product was confirmed by deamination and the synthesis of the dibenzoyl derivative.

The deamination was run as follows: 0.2 g of the amine was dissolved in dilute hydrochloric acid and, after cooling the solution to 0°, there was added to it the calculated amount of sodium nitrite, after which there was added 2 g of potassium hypophosphite (KH_2PO_2) with good stirring. The mixture was set aside for one day, after which the resulting precipitate was filtered off and washed with 3% solution of alkali and water, following which it was recrystallized from glacial acetic acid. The resulting product melted at 188°, which corresponded to the melting point of 1,8-naphthoylene-1',2'-benzimidazole [7].

The dibenzoyl derivative of the diamine, prepared by us by the Schotten-Baumann method, was a substance with red color and m. p. 238-239°; it was soluble in hot alcohol, acetic acid and pyridine, and insoluble in water.

Found %: N 10.82, 10.95. $C_{32}H_{20}O_3N_4$. Calculated %: N 11.02.

Mono- and disazo dyes — derivatives of 1,8-naphthoylene-1',2'-benzimidazole. Since 4(5?)-amino-1,8-naphthoylene-1',2'-benzimidazole is insoluble in dilute hydrochloric acid, we diazotized it by means of nitrosyl sulfuric acid: the sample of the amine was dissolved in excess concentrated sulfuric acid and to this solution there was added the calculated amount of dry sodium nitrite. The mixture was stirred well until the complete dissolution of sodium nitrite had taken place after which the solution was poured on ice. The diamino derivative of 1,8-naphthoylene-1',2'-benzimidazole was diazotized in the conventional manner by addition of the calculated amount of sodium nitrite to the hydrochloric acid solution of the amine. The coupling of the diazo compounds with H- and Chicago SS-acids was performed in an alkaline medium, which was maintained by addition of sodium carbonate. The dyes were purified by the acetate method [9] and by chromatography on aluminum oxide. The absorption maxima of the aqueous solutions of the dyes were determined with the model SF-2 m spectrophotometer.

SUMMARY

There were prepared the direct mono- and disazo dyes — derivatives of 1,8-naphthoylene-1',2'-benzimidazole; a supposition was expressed concerning the structure of these dyes.

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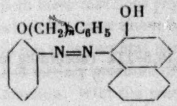
* Original Russian pagination. See C. B. translation.

REPLACEMENT OF HALOGEN IN AZO COMPOUNDS

III. PREPARATION OF DERIVATIVES OF o-ARYLALKOXYANILINES

B. I. Stepanov and M. A. Andreeva

The replacement of the chlorine atom in 2-chlorophenylazo-2'-naphthol for arylalkoxy groups is accomplished with great ease under conditions which are close to those for the replacement of chlorine by an alkoxy group [1] – in the reaction with the alcoholate in an excess of the corresponding alcohol in the presence of a copper salt at temperature about 100°. In this manner there were prepared the products of replacement of chlorine by phenylmethoxy group – by reaction with sodium benzyloxide, by β-phenylethoxy group – by reaction with sodium β-phenylethoxide, and by γ-phenylpropoxy group – by reaction with sodium γ-phenylpropoxide. The resulting arylalkoxy substituted dyes were capable of dyeing the acetate and the polyamide fibers. The corresponding o-arylalkoxyanilines were prepared by reductive cleavage of the indicated dyes.



$n = 1, 2, 3$

EXPERIMENTAL

Replacement of chlorine by phenylmethoxy-, β-phenylethoxy, and γ-phenylpropoxy groups. 8 g of the azo dye from 2-chloroaniline and 2-naphthol (m. p. 167°), triturated with 4 g of copper sulfate and 5 ml of water, was introduced into the solution of sodium alcoholate prepared by the reaction of 2 g of metallic sodium with 40 ml of the appropriate alcohol (benzyl – b. p. 204-206°; β-phenylethyl – b. p. 219-221° at 750 mm, γ-phenylpropyl – b. p. 235-237°). The mixture was heated under a reflux condenser for 8 hrs at 100-103°, after which it was diluted with 2-3 volumes of methyl alcohol. The resulting precipitate was filtered off, boiled with 100 ml of concentrated hydrochloric acid, refiltered after dilution with water, washed free of chloride ions and dried in air. The test for halogen was negative.

There was obtained 8.65 g (86.3%) of the phenylmethoxy substituted dye (I). After recrystallization from glacial acetic acid it formed bundles of small sharp needles, m. p. 152-153° (see [2]). The dye was soluble in benzene, toluene, chloroform, chlorobenzene and glacial acetic acid, poorly soluble in methyl and ethyl alcohols, and insoluble in water.

There was obtained 9.45 g of phenylethoxy substituted dye (II). After recrystallization from glacial acetic acid it formed narrow flat needles, m. p. 161°. The dye was soluble in benzene, toluene, chloroform, and glacial acetic acid, poorly soluble in methyl and ethyl alcohols, and insoluble in water.

There was obtained 7.5 g (69.3%) of the phenylpropoxy substituted dye (III). After recrystallization from 80% acetic acid, followed by ethyl alcohol, it formed bundles of plates with oval shape; m. p. 136.5-137°. The dye was soluble in benzene, toluene, and glacial acetic acid; it was less soluble in dilute acetic acid and in methyl and ethyl alcohols, and insoluble in water.

Preparation of 2-(β-phenylethoxy)- and 2-(γ-phenylpropoxy)-anilines.* 1 g of the appropriate arylalkoxy substituted dye and 25 ml of water were added to the solution of stannous chloride (prepared from 2 g of metallic tin and 25 ml of concentrated hydrochloric acid) and the mixture was refluxed until it became colorless. The

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* With participation by V. S. Zenkevich.

Substance	Found (in %)			Empirical formula	Calculated (in %)		
	C	H	N		C	H	N
(I)	77.82, 77.62	5.00, 5.20	8.11, 8.02	$C_{23}H_{18}O_2N_2$	77.97	5.09	7.91
(II)	78.04, 78.13	5.42, 5.59	7.75	$C_{24}H_{20}O_2N_2$	78.26	5.43	7.61
	78.38, 78.30	5.91, 5.72	7.50	$C_{25}H_{22}O_2N_2$	78.53	5.76	7.33
(IV)	67.30, 67.17	6.27, 6.52	5.50, 5.75	$C_{14}H_{16}ONCl$	67.33	6.41	5.61
(V)	79.92, 80.02	6.18, 6.05	4.66	$C_{21}H_{19}O_2N$	79.49	5.99	4.41
(VI)	68.24, 68.11	6.91, 6.71	5.33, 5.46	$C_{15}H_{18}ONCl$	68.31	6.83	5.31
(VII)	79.35, 79.56	6.27, 6.45	4.47	$C_{22}H_{21}O_2N$	79.76	6.34	4.23

precipitate, which formed on cooling and standing for one day, was filtered off and treated with 25 ml of 5% solution of sodium hydroxide with addition of 0.3 g of sodium hydrosulfite, after which the 2-arylalkoxyaniline was extracted with ether. After treatment of the ethereal layer with 3 ml of concentrated hydrochloric acid there formed a precipitate of the hydrochloride of the amine, which was filtered off, dried in air and recrystallized from dilute methyl alcohol. For the preparation of the N-benzoyl derivative, 0.1 g of the amine hydrochloride was treated with 1 ml of 20% solution of sodium hydroxide and 0.5 ml of benzoyl chloride, after which the mass was diluted with water, the precipitate was filtered off, washed, dried in air and recrystallized from methyl alcohol.

2-(β-Phenylethoxy) aniline hydrochloride (IV) – neeldes, m. p. 181.5-182°.

N-Benzoyl derivative of 2-(β-phenylethoxy) aniline (V) – flat rhomboids, m. p. 110.5-111° (according to literature data [3]: m. p. 113-114°, from ligroine).

2-(γ-Phenylpropoxy) aniline hydrochloride (VI) – large flat needles, m. p. 162.5-163°.

N-Benzoyl derivative of 2-(γ-phenylpropoxy) aniline (VII) – bundles of small needles, m. p. 87-87.5°.

The analytical data of the compounds prepared by us are given in the table.

SUMMARY

1. By the reaction of sodium alcoholates with the azo dye from 2-chloroaniline and 2-naphthol in the presence of a copper salt, the chlorine atom in the dye was replaced by phenylmethoxy-, β-phenylethoxy- and γ-phenylpropoxy groups.

2. 2-(β-Phenylethoxy)- and 2-(γ-phenylpropoxy) anilines were prepared by reductive cleavage of the arylalkoxy substituted dyes.

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* Original Russian pagination. See C. B. translation.

ANOMALOUS REACTION OF PHOSPHITES WITH α-HALO KETONES

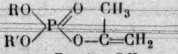
VIII. REACTIONS OF MIXED PHOSPHITES WITH CHLORO- AND DICHLOROACETONES

A. N. Pudovik and E. G. Chebotareva

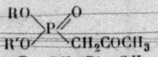
It was shown by us in previous publications that α-halo substituted ketones react with complete esters of phosphorous acid both according to the scheme of the Arbuzov rearrangement, forming esters of keto phosphonic acids, and according to the anomalous reaction route with formation of unsaturated esters of phosphoric acid [1]. Both these reactions proceed independently of each other; the ratio of their rates depends on the temperature at which the experiment is performed, the nature of the halogen and its position in the ketone molecule [2]. Lowering of the experimental temperature, change from the iodo- to bromo- and chloroketones, from primary to secondary and tertiary positions of the halogen in the molecule of the halo ketone, all favor the progress of the anomalous reaction. With the presence of more than one chlorine atom in the halo ketone at the α-position, the reactions proceed exclusively or almost exclusively according to the anomalous direction.

We set up for the goal in the present work, a study of the reaction of α-halo ketones with mixed phosphites containing aliphatic or aliphatic and aromatic radicals in the ester groups. For the α-halo ketones we used chloro- and α,α-dichloroacetones. The selection of these halo ketones was made owing to the fact that the reaction of the former with the usual phosphites proceeds predominantly anomalously, while that of the latter proceeds completely anomalously [3]. As is known, the reaction of mixed esters of phosphorous acid with alkyl halides and other halogen containing organic compounds proceeds in such a way that the radical with the smallest molecular weight is cleaved from the phosphite; there are formed the alkyl halide and an ester of a phosphonic acid. It was of some interest to determine the behavior of mixed phosphites in their reactions with α-halo ketones which proceed according to the anomalous scheme. As the mixed phosphites we utilized diisobutyl ethyl, diethyl phenyl, di-n-butyl phenyl esters and ethyl bis-(diethylamido)phosphite, $(Et_2N)_2POEt$.

The diisobutyl isopropenyl ester of phosphoric acid (I) was obtained from the reaction of chloroacetone with diisobutyl ethyl phosphite. In respect to its physical constants this substance was identical with the diisobutyl isopropenyl phosphate, prepared by us earlier from chloroacetone and triisobutyl phosphite [2]. The keto phosphonic ester, isomeric to this, was not isolated in the pure state owing to the low content of it in the reaction mixture. The constants of (I), as well as those of all the other products described below which were prepared from chloroacetone, are shown in Table 1. Two products were obtained from the reaction of chloroacetone with diethyl phenyl phosphite: phenyl ethyl isopropenyl ester of phosphoric acid (II) and phenyl ethyl ester of phosphonoacetone (III). Ethyl chloride was evolved during the reaction.



(I) $R = R' = iso\text{-}C_4H_9$
(II) $R = C_6H_5,\ R' = C_2H_5$
(IV) $R = C_6H_5,\ R' = n\text{-}C_4H_9$
(VI) $R = R' = C_6H_5$



(III) $R = C_6H_5,\ R' = C_2H_5$
(V) $R = C_6H_5,\ R' = n\text{-}C_4H_9$

Three times more of substance (II) than of substance (III) was isolated. The double bond was quantitatively determined in substance (II), while it was absent in substance (III). Acetone was obtained in 90% yield in transesterification of (II) with ethyl alcohol, run in the presence of sodium ethoxide.

TABLE 1

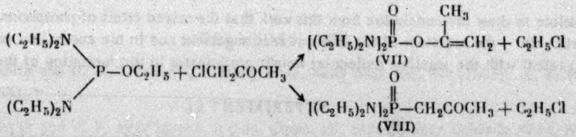
Reaction Products of the Mixed Esters with Chloroacetone

Initial ester	Reaction product	Yield (in %)	Boiling point (pressure in mm)	d_4^{20}	n_D^{20}	MR_D		Phosphorus content (%)		Content of CO (in %)		Double bond found (in %)
						found	calc.	found	calc.	found	calc.	
$(iso\text{-}C_4H_9O)_2POC_2H_5$	Diisobutyl isopropenyl phosphate (I)	69.3	122—123° (9)	0.9960	1.4245	64.15	64.52	—	—	—	—	—
$(C_2H_5O)_2POC_6H_5$	Ethyl isopropenyl phenyl phosphate (II)	58.3	151.5—152(10)	1.1423	1.4845	60.72	60.92	12.50	12.80	—	—	97.6
	Ethyl phenyl ester of phosphonoacetone (III)	17.0	178—179 (8)	1.1883	1.5005	59.99	60.27	12.43	12.80	11.53	11.56	—
$(C_4H_9O)_2POC_6H_5$	n-Butyl isopropenyl phenyl phosphate (IV)	49.2	166—167 (9)	1.1005	1.4825	70.07	70.16	11.68	11.47	—	—	96.1
	n-Butyl phenyl ester of phosphonoacetone (V)	13.3	176—177 (4)	1.1276	1.4944	69.75	69.51	11.54	11.47	10.50	10.37	—
$(C_6H_5O)_2POC_4H_9$	Diphenyl isopropenyl phosphate (VI)	57.4	186 (1.5)	1.2271	1.5483	75.15	75.79	10.22	10.68	—	—	94.2
$[(C_2H_5)_2N]_2POC_2H_5$	Isopropenyl bis-(diethylamido)-phosphate (VII)	40	124—125 (8)	0.9920	1.4520	67.53	68.23	12.69	12.50	—	—	—
	Bis-(diethylamide) of phosphonoacetone (VIII)	8.3	149—150 (8)	1.0413	1.4709	66.62	67.58	12.75	12.50	—	—	—

The reaction of chloroacetone with phenyl di-n-butyl phosphite proceeds analogously. Phenyl butyl isopropenyl ester of phosphoric acid (IV) and phenyl butyl ester of phosphonoacetone (V) were obtained. The presence of the double bond in substance (IV) was confirmed by bromination; acetone was obtained in a quantitative yield on hydrolysis of this substance with 30% sulfuric acid. The carbonyl group was determined in (V). Three times more of substance (IV) was obtained than of substance (V). n-Butyl chloride was isolated in the course of the reaction; about 85% of the theoretical amount of this substance, calculated for both the reaction products, was collected.

During the action of chloroacetone on diphenyl n-butyl ester of phosphorous acid there was obtained the diphenyl isopropyl ester (VI). The diphenyl ester of phosphonoacetone did form, but in a small amount, and could not be isolated in the pure state. Formaldehyde, identified as the product of condensation with dimethylcyclohexanedione, was obtained in ozonization of ester (VI).

The reaction of chloroacetone with the ethyl ester of bis-(diethylamido) phosphite proceeded just as readily as with the mixed phosphites. There were isolated: isopropenyl ester of bis-(diethylamido) phosphoric acid (VII) and bis-(diethylamido) phosphonoacetone (VIII). Ethyl chloride was evolved in the process of the reaction.



$$[(C_2H_5)_2N]_2P{-}OC_2H_5 + ClCH_2COCH_3 \rightarrow [(C_2H_5)_2N]_2\overset{O}{\overset{\|}{P}}{-}O{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2 + C_2H_5Cl \quad (VII)$$

$$[(C_2H_5)_2N]_2P{-}OC_2H_5 + ClCH_2COCH_3 \rightarrow [(C_2H_5)_2N]_2\overset{O}{\overset{\|}{P}}{-}CH_2COCH_3 + C_2H_5Cl \quad (VIII)$$

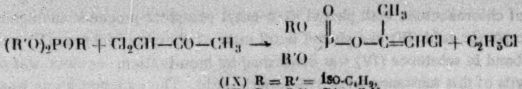
The presence of the double bond in substance (VII) was confirmed by bromination, while it was absent in substance (VIII). Five times more of substance (VII) than of substance (VIII) was isolated.

Then we studied the reactions of diisobutyl ethyl phosphite, diethyl phenyl phosphite and di-n-butyl phenyl phosphite with α,α-dichloroacetone. As in the case of the usual phosphites, the reactions proceeded in these cases solely by the anomalous route with formation of the corresponding unsaturated phosphoric acid esters.

TABLE 2

Reaction Products of Mixed Esters with α,α-Dichloroacetone

Initial ester	Reaction product	Yield (%)	Boiling point (pressure in mm)	d_4^{20}	n_D^{20}	MR_D		Phosphorus content(%)		Chlorine content (%)	
						found	calc.	found	calc.	found	calc.
$(iso\text{-}C_4H_9O)_2PO$ C_2H_5	Diisobutyl chloroisopropenyl phosphate (IX)	63.3	139.5–140°(9)	1.0855	1.4402	69.16	69.39	10.71	10.88	12.39	12.47
$(C_2H_5O)_2POC_6H_5$	Ethyl chloroisopropenyl phenyl phosphate (X)	51.5	130–131 (1)	1.2446	1.4972	65.60	65.79	11.1	11.20	12.40	12.83
$(C_4H_9O)_2POC_6H_5$	n-Butyl chloroisopropenyl phenyl phosphate (XI)	61.4	155–156 (3)	1.1800	1.4917	74.89	75.02	10.25	10.17	11.50	11.65

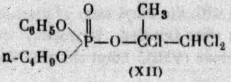


$$(R'O)_2POR + Cl_2CH-CO-CH_3 \longrightarrow (RO)(R'O)P(=O)-O-C(CH_3)=CHCl + C_2H_5Cl$$

(IX) $R = R' = iso\text{-}C_4H_9$,
(X) $R = C_6H_5$, $R' = C_2H_5$,
(XI) $R = C_6H_5$, $R' = C_4H_9$.

The constants of the products obtained (IX-XI) and the results of their analyses for the content of phosphorus and chlorine are shown in Table 2.

Trichloroisopropyl butyl phenyl ester of phosphoric acid (XII) was obtained in the chlorination of chloroisopropenyl n-butyl phenyl ester of phosphoric acid (XI).



$$(C_6H_5O)(n\text{-}C_4H_9O)P(=O)-O-CCl(CH_3)-CHCl_2$$

(XII)

It is possible to draw the conclusion from this work that the mixed esters of phosphorous acid behave similarly both in the reactions of the Arbuzov rearrangement and in the anomalous reaction with α-halo ketones; the radical with the smallest molecular weight participates in the formation of the alkyl halide.

EXPERIMENTAL

Mixed esters of phosphorous acid were prepared from the corresponding ester chlorides of phosphorous acid and alcohols, in the presence of pyridine.

The technique of running the reactions of chloro- and dichloroacetone with mixed phosphites. To 30-40 g of the mixed phosphite, placed in an Arbuzov flask and preheated to 120-140°, there was gradually added from a dropping funnel the equimolar amount of chloro- or dichloroacetone. The Arbuzov flask was connected to a distilling condenser. In cases in which ethyl chloride was evolved in the process of the reaction, this was passed through a glass tube coil cooled with a freezing mixture and collected in a receiver. After the addition of chloroacetone or dichloroacetone, the reaction mixture was heated for 1 hr longer at 120-130° after which it was distilled in vacuo from a flask with a Widmer column. The constants of all the products thus obtained and their analyses are shown in Tables 1 and 2.

Transesterification of ethyl phenyl isopropenyl esters of phosphoric acid. To a solution of sodium ethoxide, prepared in an Arbuzov flask, from 10 ml of anhydrous ethyl alcohol and 0.17 g of sodium, there was added 9.3 g of ethyl phenyl isopropenyl phosphate. After heating of the reaction mixture on a water bath, there was collected 1.9 g of acetone. Its semicarbazone had m. p. 187-188°. The mixed melting point with an authentic sample showed no depression.

Hydrolysis of n-butyl phenyl isopropenyl ester of phosphoric acid. n-Butyl phenyl isopropenyl phosphate (4.5 g) and 8 ml of 30% sulfuric acid, placed in an Arbuzov flask provided with a distilling condenser, were gradually heated on a water bath. The reaction began immediately and proceeded very vigorously with strong heat evolution within the reaction mixture. There was collected 1.5 g of acetone with b. p. 56-57°. Its semicarbazone had m. p. 188°.

Ozonolysis of diphenyl isopropenyl phosphate. Ozonized oxygen was passed for 20 hrs into a solution of 4 g of diphenyl isopropenyl phosphate in 20 ml of dry carbon tetrachloride with cooling by means of a freezing mixture. After the removal of the solvent by evacuation, the ozonide was decomposed with water, with heating on a water bath. From the distillate, which had the sharp odor of formaldehyde, there was obtained the condensation product with dimethylcyclohexanedione, with m. p. 188-189°. The mixed melting point with an authentic sample had m. p. 189°.

Chlorination of chloroisopropenyl n-butyl phenyl ester of phosphoric acid. Chlorine was slowly introduced into a solution of 6.2 g of the phosphate ester in 30 ml of dry carbon tetrachloride with cooling by means of a freezing mixture. The solution remained colorless during the process of chlorination, but turned yellow upon reaching the theoretical weight gain of 1.12 g. After distillation of the reaction mixture from a flask with a Widmer column there was obtained 4.8 g of α,β,β-trichloroisopropyl n-butyl phenyl phosphate.

B. p. 180-181° at 4 mm, d_4^{20} 1.2837, $n^{20}D$ 1.5020, MR_D 87.36; calc. 85.22. Found %: P 8.30; Cl 28.48. $C_{13}H_{18}O_4Cl_3P$. Calculated %: P 8.25; Cl 28.32.

SUMMARY

1. The reactions of chloro- and dichloroacetones with diisobutyl ethyl, diethyl phenyl, di-n-butyl phenyl, diphenyl n-butyl esters of phosphorous acid and ethyl bis-(diethylamido) phosphite were studied.

2. The reactions of chloroacetone with mixed esters proceed by two paths: by the anomalous route with formation of unsaturated phosphoric esters and by the scheme of Arbuzov rearrangement with formation of dialkyl esters of phosphonoacetone. The reactions with α,α-dichloroacetone proceed exclusively by the anomalous route with formation of unsaturated phosphoric esters.

3. In all the reactions of chloro- and dichloroacetones with mixed esters of phosphorous acid, the alkyl radical of the mixed phosphite having the smallest molecular weight takes part in the formation of the alkyl chloride.

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ADDITION OF AMMONIA AND AMINES TO ISOPRENE OXIDE

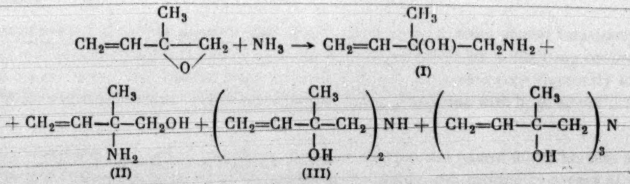
A. N. Pudovik and I. M. Aladzheva

It was shown in a paper by one of us and S. G. Denislamova [1] that isoprene oxide, in contrast to oxides of propylene [2], isobutylene [3] and butadiene [4], adds alcohols in the presence of alcoholates of the alkali metals predominantly, but not exclusively, in accord with the Markovnikov rule [5]. Some 10-14% of ethers of tertiary alcohols were isolated along with the primary ethers. It appeared interesting in connection with the previous studies to investigate the addition of ammonia and amines to isoprene oxide.

Krasusskii [6] had shown that the addition of ammonia and amines to oxides of unsymmetric ethylenic hydrocarbons – propylene, isobutylene, trimethylethylene and diethylethylene – proceeds according to the Markovnikov rule. Analogous reactions with oxides of diene hydrocarbons have not been studied sufficiently. According to the existing data, ammonia adds to butadiene oxide with formation of a mixture of both isomeric amino alcohols [7], while amines yield amino alcohols with the secondary alcohol grouping only [8]. According to the existing concepts, the order of addition of neutral or basic reagents to unsymmetric α-oxides is determined to a considerable degree by polarization of the oxide molecule and by stability of carbon-oxygen bonds in it [9]. In accord with this, one may suppose that the addition of ammonia and amines to isoprene oxide, which is an unsymmetric disubstituted oxide, would proceed in accordance with the Markovnikov rule.

We studied the addition of ammonia, ethylamine, diethylamine and aniline to isoprene oxide. In order to secure a more correct conception of the direction of the course of these reactions, these were run with considerable amounts of isoprene oxide (0.8-1.1 mole), i. e., several times larger than those used previously in analogous experiments with butadiene oxide and some other oxides.

As the result of addition of ammonia to isoprene oxide in aqueous medium there were obtained four products, of which the first two were isomeric products of addition of one molecule of ammonia to one molecule of isoprene oxide, the third was the product of addition of ammonia to two, and the fourth – to three molecules of isoprene oxide.



$$CH_2{=}CH{-}\overset{CH_3}{C}{-}CH_2\ (\text{epoxide } {-}O{-}) + NH_3 \rightarrow CH_2{=}CH{-}\overset{CH_3}{C}(OH){-}CH_2NH_2\ \text{(I)} +$$

$$+\ CH_2{=}CH{-}\overset{CH_3}{\underset{NH_2}{C}}{-}CH_2OH\ \text{(II)} + \left(CH_2{=}CH{-}\overset{CH_3}{\underset{OH}{C}}{-}CH_2\right)_2 NH\ \text{(III)} + \left(CH_2{=}CH{-}\overset{CH_3}{\underset{OH}{C}}{-}CH_2\right)_3 N$$

There was obtained approximately 4.5 times more 3-methyl-4-amino-1-buten-3-ol than 3-methyl-3-amino-1-buten-4-ol (II); it boiled 20° lower and had a lower index of refraction and specific gravity. On the basis of a quantitative comparison of the resulting isomers and their physical constants, we came to the conclusion that substance (I) was the amino alcohol with a tertiary alcohol group, i. e., the product formed in accordance with the Markovnikov rule, while substance (II) was the amino alcohol isomeric to it. The product of addition of ammonia to three molecules of isoprene oxide was not isolated in pure state. The characterization of the products obtained by us is shown in the table. The total yield of amino alcohols, calculated on the isoprene oxide taken for the reaction, was about 60%. In ozonolysis of (II) formaldehyde was identified, which fact also serves as a confirmation of the proposed structural formula and excludes the supposition about the possibility of an allylic shift in the process of reaction, changing (I) into 3-methyl-4-amino-2-buten-1-ol.

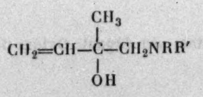
Amino Alcohols Prepared in the Reaction of Isopropene Oxide with Ammonia and Amines

Reagent	Reaction products	Yield (in %)	Boiling point (pressure in mm)	d^{20}_4	$n^{20}D$	MR_D		Nitrogen cont. (in %)	
						found	calc.	found	calc.
Ammonia	1-Amino-2-hydroxy-2-methyl-3-butene (I)	41.0	63° (9)	0.9548	1.4692	29.51	29.77	13.78	13.86
	1-Hydroxy-2-amino-2-methyl-3-butene (II)	9.1	83 (13)	0.9693	1.4772	29.50	29.77	13.75	13.86
	Bis-(2-hydroxy-2-methyl-3-butenyl)amine (III)	9.0	133.7–134.2 (14)	0.9702	1.4740	53.67	54.09	7.28	7.56
Ethylamine	1-Ethylamino-2-hydroxy-2-methyl-3-butene (IV)	44.4	51.5 (9)	0.8865	1.4462	38.88	39.18	10.64	10.85
	1-Hydroxy-2-methyl-2-ethylamino-3-butene (V)	9.3	82 (9)	0.9157	1.4598	38.63	39.18	11.04	10.85
	Bis-(2-hydroxy-2-methyl-3-butenyl)ethylamine (VI)	4.8	125–127 (14)	0.9562	1.4730	62.38	63.67	6.96	6.57
Phenylamine	1-Phenylamino-2-hydroxy-2-methyl-3-butene (VII)	–	120–124 (11)	1.0154	1.5470	55.67	56.23	8.18	7.90
	1-Hydroxy-2-phenylamino-2-methyl-3-butene (VIII)	–	137–140 (11)	1.0338	1.5670	56.35	56.23	8.19	7.90
Diethylamine	1-Diethylamino-2-hydroxy-2-methyl-3-butene (IX)	48.8	63 (13)	0.8534	1.4388	48.45	48.76	9.2	8.9
	1-Hydroxy-2-diethylamino-2-methyl-3-butene (X)	10.5	78 (12)	0.8693	1.4472	48.36	48.76	9.0	8.9

In running the reaction between isoprene oxide and ethylamine, three products were isolated: two isomeric amino alcohols formed by the addition of ethylamine to the oxide ring in both possible directions and the product of addition of ethylamine to two molecules of isoprene oxide. There was obtained 5 times more 3-methyl-4-ethylamino-1-buten-3-ol (IV) than 3-methyl-3-ethylamino-1-buten-4-ol (V). The total yield of products was about 59% (see Table).

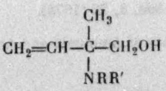
The reaction of isoprene oxide with aniline proceeds very slowly and incompletely in an aqueous medium, owing to the low solubility of aniline in water. Two isomeric amino alcohols (VII and VIII) were isolated in low yields.

Addition of a secondary amine – diethylamine – to isoprene oxide proceeded in aqueous medium as readily as that of primary amines. Five times more amino alcohol with the tertiary alcohol group (IX) was formed in comparison with its isomer (X).



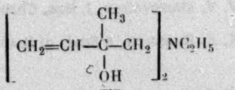
$$CH_2{=}CH{-}\underset{OH}{\overset{CH_3}{C}}{-}CH_2NRR'$$

(IV) $R = C_2H_5,\ R' = H$
(VII) $R = C_6H_5,\ R' = H$
(IX) $R = R' = C_2H_5$



$$CH_2{=}CH{-}\underset{NRR'}{\overset{CH_3}{C}}{-}CH_2OH$$

(V) $R = C_2H_5,\ R' = H$
(VIII) $R = C_6H_5,\ R' = H$
(X) $R = R' = C_2H_5$



$$\left[CH_2{=}CH{-}\underset{OH}{\overset{CH_3}{C}}{-}CH_2\right]_2NC_2H_5$$

(VI)

The characterization of the prepared substances is given in the Table.

Formation of two isomeric amino alcohols in all the reactions studied by us indicates that the addition of ammonia and amines to isoprene oxide proceeds not only in accordance with the Markovnikov rule, but also to a considerable degree (about $^1/_5$) contrary to it, i. e., according to an anomalous reaction. Approximately twice as much anomalous products of addition was formed in the reactions studied by us as compared with the amount of anomalous products formed in the reactions of isoprene oxide with alcohols, in the presence of alcoholates [1].

For realization of an alternate synthesis of the amino alcohols, we ran the reaction of isoprene oxide with hydrogen chloride to prepare the original chlorohydrin. The reaction proceeded in an ethereal solution with cooling. We failed to isolate the chlorohydrin in the pure state; along with a considerable amount of tar there was isolated a small fraction with b. p. 53-58° at 13 mm, $n^{20}D$ 1.4732, d_4^{20} 1.0853, which rapidly darkened in air. The chlorine content in this fraction (in two experiments) differed from that calculated for the chlorohydrin by 2-3%. No individual product could be isolated after its reaction with ammonia. In experiments on addition of hydrobromic acid to isoprene oxide, the latter isomerized into tiglic aldehyde [10].

The results obtained by us on the addition of alcohols to isoprene oxide in the presence of alcoholates of the alkali metals, as well as of ammonia and amines, lead to the conclusion that considerable differences exist in the behavior of the oxide of isoprene as compared to oxides of isobutylene and butadiene under analogous conditions. It is necessary to add, however, that for a more correct conception of the course of the reactions of unsymmetric α-oxides with nucleophilic reagents in a basic medium, it would be rational to repeat some of the reactions run previously, to repeat them with considerably greater amounts of reagents.

EXPERIMENTAL

Isoprene α-oxide was prepared by oxidation of isoprene with acetyl hydroperoxide in ethereal solution [11]; b. p. 79-81°, $n^{20}D$ 1.4172.

Isoprene oxide (70-90 g) was added dropwise with energetic stirring by a mechanical stirrer to a three-fold (molar) excess of ammonia or amine, dissolved in water. The stirring was usually continued for one day until the oxide layer dissolved completely. (A considerable amount of aniline and oxide failed to react in the reaction with aniline). Ammonia or amine was at first distilled from the solution by gentle heating, after which water distillation was performed in vacuo. The residue was fractionated from a flask with a small Widmer column. The individual fractions, obtained in small amounts, were distilled from flasks with a shortened Widmer column. The constants, analytical results and yields of the products obtained by us are shown in the table.

SUMMARY

1. It was shown that ammonia, ethylamine and diethylamine add to isoprene oxide predominantly but not exclusively in accordance with the Markovnikov rule. About 20% of amino alcohols containing a primary alcoholic group is formed in comparison with the amount of amino alcohols which contain the tertiary alcoholic group.

2. Products of addition of ammonia and amines to isoprene oxide were obtained and characterized.

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THE PROBLEM OF SYNTHESIS OF DI-β,β'-CHLOROETHYL ESTER OF VINYLPHOSPHONIC ACID

E. L. Gefter

Esters of vinylphosphonic acid are rather reactive compounds, capable of polymerization [1, 2], addition of substances with a mobile hydrogen to the double bond [3-5], participation in diene synthesis [6], etc. One of the insufficiently studied compounds in this series, which became industrially important recently [7], is bis-β,β'-chloroethyl ester of vinylphosphonic acid, prepared first by M. I. Kabachnik [1] by the reaction of alcoholic alkali with bis-β,β'-chloroethyl ester of β-chloroethylphosphonic acid. However, this method has a material defect: along with the cleavage of hydrogen chloride, some hydrolysis of the ester takes place, which fact sharply lowers the yields of the ester of vinylphosphonic acid.

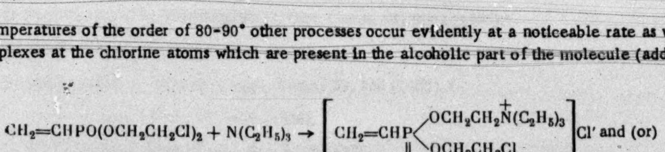
In order to raise the yields of bis-β,β'-chloroethyl vinylphosphonate we used as dehydrochlorinating agent the triethylamine which was first used by Ford-Moore and Williams [8] in the preparation of diethyl vinylphosphonate by the principle mentioned above. Since the halogen in the β-haloethyl group bound directly to phosphorus is more active than the halogen in a similar group bound to phosphorus through oxygen [1], we supposed that the dehydrochlorination should occur only in the acidic part of the molecule of bis-β,β'-chloroethyl ester of β-chloroethylphosphonic acid. However, it appeared that this process proceeds in a more complex manner. Along with the expected reaction product – bis-β,β'-chloroethyl vinylphosphonate – obtained in 50-60% yields, there also remained always a certain amount of unreacted starting material. In case of utilization of an excess of triethylamine (up to 20% of theoretical), the yields of bis-β,β'-chloroethyl vinylphosphonate declined. It was possible to suppose that the reaction of bis-β,β'-chloroethyl ester of β-chloroethylphosphonic acid with triethylamine proceeds in two steps.

1) Formation of an unstable complex or quaternary ammonium salt (addition product I) (formation of complexes in the reactions of tertiary amines with various halogen containing compounds has been described [9, 10]). 2) Facile cleavage of product (I):

$$\mathrm{ClCH_2CH_2PO(OCH_2CH_2Cl)_2 + N(C_2H_5)_3 \rightarrow Cl'\underset{(I)}{[(C_2H_5)_3N{-}CH_2CH_2PO(OCH_2CH_2Cl)_2]} \rightarrow}$$

$$\mathrm{\rightarrow CH_2{=}CHPO(OCH_2CH_2Cl)_2 + N(C_2H_5)_3 \cdot HCl}$$

At temperatures of the order of 80-90° other processes occur evidently at a noticeable rate as well; formation of complexes at the chlorine atoms which are present in the alcoholic part of the molecule (addition product II):



$$\mathrm{CH_2{=}CHPO(OCH_2CH_2Cl)_2 + N(C_2H_5)_3 \rightarrow \left[CH_2{=}CH\underset{\overset{\|}{O}}{P}\begin{matrix}OCH_2CH_2\overset{+}{N}(C_2H_5)_3\\OCH_2CH_2Cl\end{matrix}\right]Cl'}\text{ and (or)}$$

$$\mathrm{ClCH_2CH_2PO(OCH_2CH_2Cl)_2 + N(C_2H_5)_3 \rightarrow \left[ClCH_2CH_2\underset{\overset{\|}{O}}{P}\begin{matrix}OCH_2CH_2\overset{+}{N}(C_2H_5)_3\\OCH_2CH_2Cl\end{matrix}\right]Cl'}$$

(II)

Compounds of type (II) are rather stable [11] and under the reaction conditions may simply precipitate, thus leaving the reaction zone. (Analysis showed the admixture of organophosphorus compounds in the triethylamine hydrochloride.) As a result of such secondary processes, the yields of bis-β,β'-chloroethyl vinylphosphonate should decline naturally, while a part of the starting material would remain unchanged since no free triethylamine would be present in the system.

We supposed that an elevation of the temperature of the system should aid the formation of all the complexes listed above, while low temperature in the initial stage would aid the progress of only the main process. This supposition was confirmed. Thus, the convenient method of preparation of bis-β,β'-chloroethyl ester of vinylphosphonic acid turned out to be the slow heating of a mixture of bis-β,β'-chloroethyl ester of β-chloroethylphosphonic acid and triethylamine (in molar ratio of 1 : 1.02) in a benzene solution. The precipitate of triethylamine hydrochloride was removed as completely as possible (see experimental part), and bis-β,β'-chloroethyl vinylphosphonate was fractionated in vacuo. The yield was about 70% of theoretical. We should note that the admixture of triethylamine hydrochloride (if this is not washed out completely) during the distillation suffers a partial decomposition and is partially drawn into the distillate. Pure bis-β,β'-chloroethyl ester of vinylphosphonic acid distills without decomposition.

The above-described method, in connection with the previously developed method of safe preparation of bis-β,β'-chloroethyl ester of β-chloroethylphosphonic acid [12], makes di-β,β'-chloroethyl vinylphosphonate a readily available substance.

EXPERIMENTAL

The initial bis-β,β'-chloroethyl ester of β-chloroethylphosphonic acid was prepared by the previously described method [12].

Preparation of bis-β,β'-chloroethyl vinylphosphonate. (One of typical experiments.) A mixture of 1080 g of bis-β,β'-chloroethyl ester of β-chloroethylphosphonic acid, 412 g of triethylamine and 1000 ml of benzene, protected from atmospheric moisture, was stirred for 3 hrs at 30-40°, 2 hrs at 50-60° and 3 hrs at 80-85°. The resulting precipitate of triethylamine hydrochloride was filtered off on the following day and washed with benzene. Benzene was distilled from the filtrate. The residue, from which some crystals had precipitated again, was filtered, the filtrate was washed with water and fractionated at 3-4 mm. There were obtained the following fractions: 1st, with b. p. 22-135°; 2nd with b. p. 135-146°, 591 g; 3rd with b. p. 146-161°, 135 g. After repeated distillation of the second and the third fractions there was obtained 601 g of bis-β,β'-chloroethyl vinylphosphonate (yield with account being taken of recovery of the starting material was 70% of theoretical) and 80 g of unreacted bis-β,β'-chloroethyl ester of β-chloroethylphosphonic acid.

B. p. 131-132° (3 mm), 135-137° (4 mm), $n^{20}D$ 1.4787, d_4^{20} 1.3233, MR_D 49.91; calc. 50.13 (in the calculation we used the atomic increment values cited in [13]).

Found %: P 13.3; Cl 30.8. $C_6H_{11}O_3PCl_2$. Calculated %: P 13.3; Cl 30.5.

With a rapid running of the reaction with the same molar ratios of the components, the yields of bis-β,β'-chloroethyl vinylphosphonate dropped by 10-12%. Bis-β,β'-chloroethyl ester of vinylphosphonic acid was a colorless transparent liquid, soluble in benzene, toluene, alcohol and ether, insoluble in water.

SUMMARY

The method of preparation of bis-β,β'-chloroethyl ester of vinylphosphonic acid in yields of about 70% of theoretical was described.

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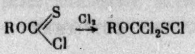
* Original Russian pagination. See C. B. translation.

A NEW METHOD OF INTRODUCTION OF TRIHALOMETHYL GROUP INTO ORGANIC COMPOUNDS

N. N. Iarovenko and A. S. Vasil'eva

The goal of the present work was the search for a method of replacement of hydrogen in a hydroxyl group in an organic compound by a trifluoromethyl group: $ROH \rightarrow ROCF_3$. It is known that certain dyes containing the polyfluoroalkoxyl group, for example, CF_3CH_2O, possess interesting properties [1]. Dyes containing the trifluoromethoxyl group have been studied but little up to the present time [2].

A new method for introduction of the trihalomethyl group into organic compounds was discovered during a study of chemical properties of phenyl ester of chlorothiocarbonic acid (see also [3]). We showed that this compound is capable of readily adding two atoms of chlorine with formation of phenoxydichloromethylenesulfenyl chloride:



$$ROC(=S)Cl \xrightarrow{Cl_2} ROCCl_2SCl$$

Upon further chlorination, the sulfur is completely eliminated in the form of chlorides of sulfur and there is formed trichloromethyl phenyl ether:

$$ROCCl_2SCl \xrightarrow{Cl_2} ROCCl_3$$

Fluorination of this ether proceeds very readily. Difluorochloromethyl phenyl ether was obtained on heating trichloromethyl phenyl ether with antimony trifluoride without a catalyst. The reaction begins after a slight heating and proceeds quietly in a usual glass flask. A deeper fluorination of trichloromethyl phenyl ether does not occur without a catalyst even at 200°, but should one add a small amount of antimony pentachloride, the spontaneously progressing exothermic fluorination to trifluoromethyl phenyl ether takes place.

$$C_6H_5OCCl_3 \xrightarrow{SbF_3} C_6H_5OCF_2Cl$$

$$C_6H_5OCF_2Cl \xrightarrow{SbF_3+SbCl_5} C_6H_5OCF_3$$

EXPERIMENTAL

Trichloromethyl phenyl ether. 20 g of phenyl ester of chlorothiocarbonic acid was saturated with chlorine with simultaneous cooling with ice water, until the weight gain of chlorine reached 8.25 g. Then the reaction mixture was washed with water and dried with calcium chloride. The yield of phenoxydichloromethylenesulfenyl chloride was 21 g (74.5%). The substance was a yellow liquid with an odor characteristic of alkylsulfenyl chlorides. It was insoluble in water. It dissolved readily in ether and chloroform. It decomposed on attempted distillation; d_4^{19} 1.4306, $n^{19}D$ 1.5690.

Found %: Cl 44.49; S 13.09. $C_7H_5OCl_3S$. Calculated %: Cl 43.80; S 13.16.

The product (8.5 g) was saturated with chlorine at 40-45° until the weight gain of chlorine reached 2.5 g. The sulfur chlorides were distilled and the trichloromethyl phenyl ether was distilled at 108-110° (16 mm). The yield of trichloromethyl phenyl ether was 7 g (95%), d_4^{15} 1.406, $n^{15}D$ 1.5395. (Preparation of trichloromethyl phenyl ether from phenyl ester of chlorothiocarbonic acid may be run in one step without isolation of the intermediate substance.) The compound was a colorless liquid with an unplesant odor. It does not dissolve in water, but is readily soluble in ether and chloroform.

Found %: C 39.45; H 2.64; Cl 49.41. $C_7H_5OCl_3$. Calculated %: C 39.81; H 2.37; Cl 50.00.

Difluorochloromethyl phenyl ether. In a glass flask there was mixed 11 g (0.062 mole) of antimony trifluoride and 13 g (0.062 mole) of trichloromethyl phenyl ether and the mixture was heated slowly to 75°. After 10-15 min following the completion of the reaction, the liquid products were distilled at the pressure of 90-100 mm, washed with dilute hydrochloric acid and, after drying with calcium chloride, again distilled at 71° (58 mm). The yield of difluorochloromethyl phenyl ether was 6 g (52%); d_4^{18} 1.2748, $n^{18}D$ 1.4518. The product was a colorless liquid. It was insoluble in water, but dissolved readily in the usual organic solvents.

Found %: C 47.92; H 2.84; Cl 20.49; F 21.94. $C_7H_5OF_2Cl$. Calculated %: C 47.20; H 2.81; Cl 19.90; F 21.35.

Trifluoromethyl phenyl ether. To a mixture of 5 g of antimony trifluoride with 0.5 g of antimony pentachloride there was added with stirring 3 g of difluorochloromethyl phenyl ether. After termination of heat evolution of the mixture, the liquid reaction products were distilled at atmospheric pressure, washed with water, dried with calcium chloride and redistilled. The yield of trifluoromethyl phenyl ether was 3.2 g (71%).

By an analogous method there was obtained from 17 g of antimony trifluoride mixed with 2 g of antimony pentachloride and 80 g of trichloromethyl phenyl ether, 11.1 g of trifluoromethyl phenyl ether. Yield: 53%. B. p. 104°, d_4^{21} 1.2800, $n^{21}D$ 1.4073.

Found %: C 51.81; H 3.16; F 35.29. $C_7H_5OF_3$. Calculated %: C 51.80; H 3.08; F 35.11.

SUMMARY

1. A new and simple method was proposed for the introduction of a trihalomethyl group into organic compounds, the method consisting of introduction of halothiocarbonyl group into an organic molecule, with a subsequent chlorination of the latter to the trihalomethyl form.

2. Trichloromethyl, difluorochloromethyl and trifluoromethyl phenyl ethers were prepared for the first time by the above method.

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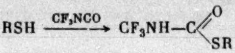
PREPARATION OF ESTERS OF N-TRIFLUOROMETHYLTHIOLCARBAMIC ACID

N. N. Iarovenko and S. P. Motornyi

Chemistry of fluoroalkylisocyanates began its history with the work of Hückel, who in 1946 prepared mono-, di- and trifluoromethylisocyanates [1]. After Hückel, a considerable number of new fluoroalkylisocyanates were prepared and their properties studied to some degree. Thus, for example, there were published the studies of addition of methyl alcohol and some phenols to perfluoroalkylisocyanates, reactions with water, with ammonium hydroxide, with alcoholic solution of sodium hydroxide, with acetic acid [2, 3]. Recently we discovered and described a new reaction which permits one to prepare halides of the previously unknown N-trifluoromethylcarbamic acid [4].

In light of these studies a considerable interest exists in the study of reactions of perfluoroalkylisocyanates with organic compounds, containing the sulfhydryl groups. In the present work we investigated the reactions of trifluoromethylisocyanate with methyl and phenyl mercaptans. As presupposed, perfluoroalkylisocyanates readily enter into reaction with mercaptans, forming esters of N-perfluoroalkylthiolcarbamic acids:



$$RSH \xrightarrow{CF_3NCO} CF_3NH{-}C\begin{smallmatrix}\nearrow O\\ \searrow SR\end{smallmatrix}$$

EXPERIMENTAL

Methyl ester of N-trifluoromethylthiolcarbamic acid. Into a glass ampule of 30 ml capacity there was placed 1.5 g of methyl mercaptan and, with cooling of the ampule with liquid nitrogen, 3.6 g of trifluoromethylisocyanate was condensed in it. After being sealed, the ampule was warmed to room temperature, at which an energetic reaction began. During this reaction, the ampule was periodically immersed in liquid nitrogen. After completion of the reaction, the product in the form of colorless crystals was removed from the ampule; this corresponded by analysis to methyl ester of N-trifluoromethylthiocarbamic acid. Yield was 3.6 g (63%).

Found %: N 9.09; F 35.72; S 19.63. $C_3H_4F_3ONS$. Calculated %: N 8.80; F 35.84; S 20.12.

Phenyl ester of N-trifluoromethylthiolcarbamic acid. Into a glass ampule of 30 ml capacity there was placed 1.7 g of thiophenol and, with cooling of the ampule with liquid nitrogen, 1.8 g of trifluoromethylisocyanate was condensed in it. After being sealed, the ampule was warmed to room temperature at which the reaction proceeded in the course of one hour without heat evolution. Then the ampule was heated for 1 hr at 50°. After completion of the reaction the solid product was removed from the ampule. The distilled product corresponded in its analysis to the phenyl ester of N-trifluoromethylthiolcarbamic acid. The substance formed colorless crystals. M. p. 116°; sublimation temperature 140° (at 2 mm). The yield was 1.9 g (50%).

Found %: N 6.97; F 25.62; S 14.91. $C_8H_6NF_3OS$. Calculated %: N 6.63; F 25.79; S 14.48.

SUMMARY

1. The reaction of trifluoromethylisocyanate with methyl and phenyl mercapatans was studied.
2. The corresponding esters of N-trifluoromethyithiolcarbamic acid were isolated and characterized.

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PROPERTIES OF HETEROORGANIC COMPOUNDS IN THE LIGHT OF D. I. MENDELEEV'S PERIODIC SYSTEM

I. BOILING POINTS OF COMPOUNDS OF FLUORINE AND OTHER HALOGENS

N. N. Iarovenko

In connection with the boiling points of organic compounds of fluorine an erroneous opinion is widespread to the effect that "fluorine exerts an effect on boiling points of organic compounds which is completely different from that expected by analogy with other halogens."*

Such a conclusion in respect to organofluorine compounds is totally untrue.

Fluorine, like many other elements, affects the boiling point of organic compounds in complete agreement with its position in the periodic system of the elements.

By comparison of the boiling points of analogous fluorine, chlorine and bromine organic compounds we have established that the ratio of the differences of boiling points $(t_{Cl} - t_F)/(t_{Br} - t_{Cl})$ varies within small range of limits and on the average does not differ much from 1.7 (see the table).

t_F	t_{Cl}	t_{Br}	$\frac{t_{Cl} - t_F}{t_{Br} - t_{Cl}}$
$F_2 = -188°$	$Cl_2 = -33.9°$	$Br_2 = 58.7°$	1.66
$CH_3F = -78.2$	$CH_3Cl = -23.7$	$CH_3Br = 4.5$	1.92
$CH_2F_2 = -51.6$	$CH_2Cl_2 = 41.6$	$CH_2Br_2 = 97$	1.68
$CHF_3 = -82.2$	$CHCl_3 = 61.2$	$CHBr_3 = 151.2$	1.59
$CF_4 = -128$	$CCl_4 = 76.8$	$CBr_4 = 189.5$	1.82
$C_6H_5F = 85$	$C_6H_5Cl = 132$	$C_6H_5Br = 156$	1.92
$COF_2 = -83$	$COCl_2 = 12$	$COBr_2 = 64$	1.83

The physical meaning of this coefficient consists of the fact that it represents the result of division of the difference of atomic refractions of chlorine and fluorine by the difference of atomic refractions of bromine and chlorine.

$$\frac{AR_{Cl} - AR_F}{AR_{Br} - AR_{Cl}} = \frac{5.967 - 1.0}{8.865 - 5.967} = 1.71.$$

Assuming the variation for atomic refraction of fluorine from 0.6 to 1.35, one obtained with $AR_F = 0.6$

$$\frac{AR_{Cl} - AR_F}{AR_{Br} - AR_{Cl}} = 1.85$$

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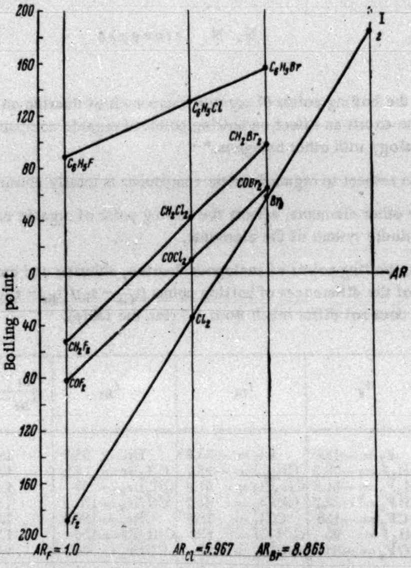
* A. G. Sharpe and R. N. Haszeldine, Fluorine and Its Compounds (London-New York, 1950).

and for $AR_F = 1.35$

$$\frac{AR_{Cl} - AR_F}{AR_{Br} - AR_{Cl}} = 1.59.$$

Consequently, the replacement of one halogen by another in various compounds changes the boiling point by different amounts, but the ratio $\frac{t_{Cl} - t_F}{t_{Br} - t_{Cl}}$ remains almost constant and equal to $\frac{AR_{Cl} - AR_F}{AR_{Br} - AR_{Cl}}$.

In order to simplify the calculation of boiling points of unknown organofluorine compounds with the above formula, it is possible to construct a graph for the use of which one does not need to make any arithmetic operations.



Graphic calculation of boiling points of halogen compounds.

For this purpose we draw parallel lines in respect to the temperature scale at distances equal to the atomic refractions of fluorine, chlorine and bromine and on these straight lines we lay off the known boiling points of bromine and chlorine compounds. Then, on the fluorine line one can read off the boiling points of the unknown fluorine compounds.

For an example on the above graph there is shown the calculation of the boiling points of fluorobenzene, difluoromethane and carbonyl fluoride.

It is evident that with this graph one may calculate the boiling points of not only fluorine compounds, but also those of chlorine, bromine and iodine organic compounds.

For computation of the boiling points of iodoorganic compounds it is necessary to expand the graph by one more straight line parallel to the temperature scale. The distance from this line to the temperature scale is somewhat smaller than the atomic refraction of iodine (12.9 instead of 13.9).

Below are shown the boiling points, found and calculated by the graph, for some organochlorine compounds.

Halomethanes

CH_3 —23.7°, calc. —26°(from CH_3F — 78.2° & CH_3Br 4.5°)
CH_2Cl_2 41.6, " 43 (" CH_2F_2—51.6 & CH_2Br_2 97)
$CHCl_3$ 61.2°, " 66 (" CHF_3—82.2 & $CHBr_3$ 151.2)
CCl_4 76.74°, " 74 (" CF_4—128 & CBr_4 189.5)

Haloethanes

CH_3CH_2Cl 12.2°, calc. 11°(from CH_3CH_2F — 37° & CH_3CH_2Br 38°)
CH_2ClCH_2Cl 83.5, " 85 (" CH_2FCH_2F 10 & CH_2BrCH_2Br 129)
CH_3CHCl_2 59.2, " 60 (" CH_3CHF_2 —24.7 & CH_3CHBr 108)
$CH_2ClCHCl_2$ 114, " 115 (" CH_2FCHF_2 5 & $CH_2BrCHBr_2$ 188)

Haloethylenes

$CH_2{=}CHCl$ —12°, calc. —16°(from $CH_2{=}CHF$—72.2 & $CH_2{=}CHBr$ 16°)
$CHCl{=}CCl_2$ 88, " 85 (" $CHF{=}CF_2$—51 & $CHBr{=}CBr_2$ 164°)
$CCl{=}CCl_2$ 121, " 117° (" $CF_2{=}CF_2$—78.4 & $CBr_2{=}CBr_2$ 227°)

Halopropylenes

$CF_3{-}CH{=}CHCl$ 21°, calc. 20°(from $CF_3{-}CH{=}CHF$—16° & $CF_3{-}CH{=}CHBr$ 40°)

Halogenated alcohols

CH_2ClCH_2OH 132°, calc. 133°(from CH_2FCH_2OH 103.35° & CH_2BrCH_2OH 150°)
$CHCl_2CH_2OH$ 146, " 148 (" CHF_2CH_2OH 96 & $CHBr_2CH_2OH$ 179)

Halogenated aldehydes

CCl_3COH 97.6°, calc. 102°(from CF_3COH —20° & CBr_3COH 174°

Halogenated acids

CH_2ClCO_2H 185—187°, calc. 184°(from CH_2FCO_2H 165° & CH_2BrCO_2H 196°)
$CHCl_2CO_2H$ 194.4°, " 195 (" CHF_2CO_2H 134.2 & $CHBr_2CO_2H$ 232 with decomp.)

Halogenated acyl halides

$CH_2ClCOCl$ 105°, calc. 113°(from CH_2FCOF 52° & $CH_2BrCOBr$ 149°)
CF_3COCl —27, " —26 (" CF_3COF —59° & CF_3COBr —5)

We also list the boiling points of some iodoorganic compounds:

CH_3I 43°, calc. 43°(from CH_3Cl —23.7° & CH_3Br 4.5°)
CF_3I —22,5, " —24 (" CF_4 —128 & CF_3Br —57.8)
C_2F_5I 13, " 15 (" C_2F_6 78 & C_2F_5Cl —38)
$CF_3CH{=}CHI$ 70—71, " 67 (" $CF_3TC{=}CHCl$ 21 & $CF_3CH{=}CHBr$ 40)
$CHFI\,CO_2C_2H_5$ 180, " 178 (" $CHF_2CO_2C_2H_5$ 99 & $CHFBrCO_2C_2H_5$ 154).

It should be noted that in some cases one may obtain an approximate notion by means of the graph concerning the boiling points of inorganic compounds as well. However, for many inorganic compounds, such as for example, hydrogen fluoride, arsenic trifluoride, cadmium fluoride, and others, there is observed a considerable deviation of the actual boiling points from those calculated by means of the graph, which fact is explained by association of the molecules of these compounds. Nevertheless even in these cases the boiling points of chlorine, bromine and iodine compounds are interconnected with atomic refractions of the halogens.

Below are shown the boiling points, both found and calculated from the graph, for some inorganic halides.

Halides of elements of Group I

HBr —68.7°, calc.— 65°(from HCl — 85° & HI —35.7°)
LiBr 1310, " 1310 (" LiCl 1382 & LiI 1189)
NaBr 1395, " 1370 (" NaCl 1413 & NaI 1300)
KCl 1415, " 1420 (" KF 1505 & KBr 1380)
KI 1319, " 1320 (" KF 1505 & KBr 1380)
Cu_2Br_2 1345, " 1335 (" Cu_2Cl_2 1366 & Cu_2I_2 1290)
RbCl 1385, " 1370 (" RbF 1410 & RbBr 1345)

Halides of elements of Group II

$ZnBr_2$ 650°, calc. 680°(from $ZnCl_2$ 732° & ZnI_2 624°)
$CdBr_2$ 810, " 810 (" $CdCl_2$ 900 & CdI_2 710)
$HgBr_2$ 325, " 320 (" $HgCl_2$ 301 & HgI_2 349)

Halides of elements of Group III

BBr_3 90°, calc . 95°(from BCl_3 12.5° & BI_3 210°)
$AlBr_3$ 260, " 266 (" $AlCl_3$ 183 & AlI_3 382)
$GaBr_3$ 278.8, " 260 (" $GaCl_3$ 201 & GaI_3 345, sublim.)

Halides of elements of Group IV

$SiBr_4$ 153°, calc. 155°(from $SiCl_4$ 57.6° & SiI_4 290°)
$SiHBr_3$ 111.8, " 111 (" $SiHCl_3$ 33 & $SiHI_3$ 220)
$TiBr_4$ 230, " 230 (" $TiCl_4$ 135.4 & TiI_4 360)
$GeBr_4$ 186.5, " 204 (" $GeCl_4$ 83.1 & GeI_4 375)
$SnBr_4$ 201, " 206 (" $SnCl_4$ 113.0 & SnI_4 340)
$SnBr_2$ 619, " 650 (" $SnCl_2$ 603 & SnI_2 720)

Halides of elements of Groups V and VI

$POCl_3$ 107.23°, calc. 115°(from POF_3 —40° & $POBr_3$ 193°)
$AsBr_3$ 221, " 242 (" $AsCl_3$ 130 & AsI_3 400)
$NbCl_5$ 240.5, " 254 (" NbF_5 229 & $NbBr_5$ 270)
$BiBr_3$ 453, " 470 (" $BiCl_3$ 447 & BiI_3 500)
$SeOCl_2$ 179.4, " 183 (" $SeOF_2$ 124 & $SeOBr_2$ 217)

Not any less interesting is the calculation of boiling point of elemental fluorine from the boiling points of chlorine and bromine:

F_2 − 188°, calculated −189° (from Cl_2 − 33.9° and Br_2 58.7°).

In following communications it will be shown that by an analogous manner one is able to approximately calculate the boiling points of heteroorganic compounds of some other groups of the periodic system, as for example, the boiling points of organic compounds of sulfur from the boiling points of analogous selenium and oxygen compounds, the boiling points of organophosphorus compounds from the boiling points of analogous nitrogenous and arsenic compounds and some others.

SUMMARY

On the basis of generalization of data on the effect of fluorine and some other elements on the boiling point of organic and inorganic compounds there was brought out a new relationship between the boiling points and atomic refraction of elements entering their compositions, and a simple method of calculation of boiling points of new compounds was suggested.

Received July 29, 1957

STUDIES IN THE FIELD OF ISOQUINOLINECARBOXYLIC ACIDS

I. PREPARATION OF 7,8-DIMETHOXYISOCARBOSTYRYL-3-CARBOXYLIC ACID, ITS ESTERS AND 7,8-DIMETHOXYISOCARBOSTYRYL

L. I. Linevich

In the group of isoquinoline compounds one meets a great number of physiologically active substances, many of which have found an area of application as medicinal substances. The acids of this series remain an insufficiently studied and difficultly accessible group of isoquinoline compounds; only a few of its representatives have been described in the literature and the data on the biological activity of these substances are very limited. Therefore, a study of this group of isoquinoline compounds and, specifically, the development of methods for their synthesis present some interest. To the study of acids of isoquinoline series one is also drawn by the fact that among derivatives of acids, close to these in structure, of the pyridine and quinoline series, many have found an application in medicine (phthivaside, cordiamine, nupercaine).

Our problem consisted of the development of methods of preparation of a series of alkoxy substituted acids of the isoquinoline group, as well as some of their derivatives, from readily accessible raw materials – opianic acid (5,6-dimethoxy-o-aldehydobenzoic acid), which is a waste product in the production and treatment of opium alkaloids. For preparation of carboxylic acids of the isoquinoline series from opianic acid, the first step of the synthesis consists of the preparation of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid, to the development of which synthesis the present paper is devoted. The development of a convenient method, for the preparative purposes, of synthesis of this acid, as well as its esters, affords the possibility of realizing various syntheses of a whole series of isoquinoline derivatives, using these substances as starting materials.

Two methods of preparation of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid are described in the literature starting with difficultly accessible methyl ester of opianic acid, but neither of these methods assures a good yield [1, 2]. By introducing several changes into Bain's method [1] we realized the synthesis of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid according to the scheme shown below with attainment of a high over-all yield of acid (III) (see diagram at top of following page).

For the starting material we used not the difficultly obtainable α-methyl ester of opianic acid, but the α-benzyl ester (I) which is readily obtained by method [3] from the potassium salt of opianic acid and benzyl chloride. Following the directions of [4] we raised the amount of benzyl chloride used in the reaction. This permitted us to raise the yield of the ester from 60% to nearly quantitative. In the condensation of α-benzyl ester (I) with hippuric acid under conditions under which Bain and co-workers obtained oxazolone from α-methyl ester of opianic acid [1], there is obtained 2-phenyl-4-(o-carboxybenzyl-m,p-dimethoxybenzal)-5-oxazolone (II) in a low yield (40-45%).* By introduction of potassium carbonate salts [5] into the reaction mixture we succeeded in raising the yield of oxazolone by a factor of two, i. e., to 85%.

The oxazolone (II) prepared by us had not been previously described; just like the oxazolone described by Bain and co-workers [1], it is readily hydrolyzed on being boiled with a solution of caustic alkali. The total yield of acid (III) in its preparation by the above-described method was about 80%, calculated on the original potassium salt of opianic acid. For characterization of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid (III) and

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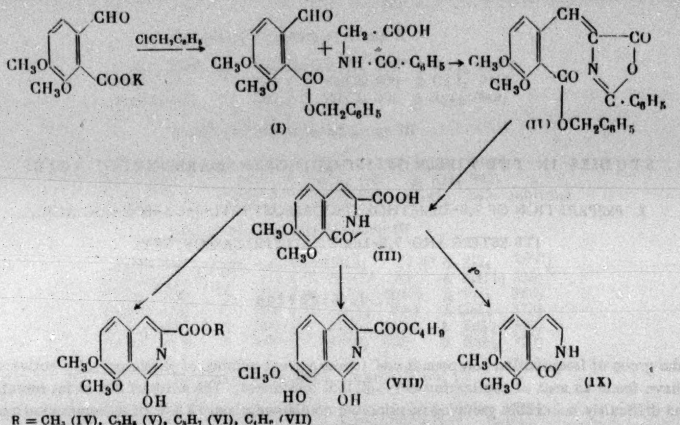
* The given oxazolone was prepared by the same method by student O. O. Evdokov.



(I)
(II)
(III)
(VIII)
(IX)
$ClCH_2C_6H_5$
R = CH_3 (IV), C_2H_5 (V), C_3H_7 (VI), C_4H_9 (VII)

for the further preparative work, there was prepared a series of its esters: methyl, ethyl, propyl and butyl (IV)-(VII), among which the last two had not been previously described. The esters were obtained in satisfactory yields on heating of the acid with alcohols and sulfuric acid. For preparation of the butyl ester the temperature must not be allowed to rise in the reaction mixture above 70°. At higher temperatures there occurs, besides the esterification, a cleavage of one of the methoxyl groups from the isoquinoline nucleus and there is formed the butyl ester of (7 ?)-methoxy-(8 ?)-hydroxyisocarbostyryl-3-carboxylic acid (VIII), which had not been described previously in the literature.

The reaction of decarboxylation was run with 7,8-dimethoxyisocarbostyryl-3-carboxylic acid, as the result of which there was obtained some 7,8-dimethoxyisocarbostyryl (IX) – a substance which is a convenient material for synthesis of a series of isoquinoline compounds which do not contain a carboxyl group.

EXPERIMENTAL

Preparation of α-benzyl ester of opianic acid (I). Into a round-bottomed flask, provided with a mechanical stirrer and a reflux condenser, connected to a calcium chloride tube, there was placed 24.8 g of finely powdered anhydrous potassium salt of opianic acid * and 75 ml of benzyl chloride. With constant stirring the mixture was heated on an oil bath to 130-150° over 1.5 hr. After cooling, the reaction mixture was filtered. Benzyl chloride was distilled in vacuo from the filtrate. The residue which was the α-benzyl ester of opianic acid (I), crystallized on cooling. Its yield was 29.9 g (99.7%). M. p. 82-83° (from alcohol) (82-83° [3]).

Preparation of 2-phenyl-4-(o-carboxybenzyl-m,p-dimethoxybenzal)-5-oxazolone (II). 3 g of α-benzyl ester of opianic acid, 1.79 g of hippuric acid and 1.38 g of potassium carbonate (or the equivalent amount of potassium bicarbonate) were powdered finely and mixed. To the mixture which had been placed into a flask, there was added 3.7 ml of acetic anhydride, the flask was stoppered with a cork carrying a calcium chloride tube and a thermometer reaching the bottom of the flask, and the reaction mixture was shaken energetically. The reaction was run without any external heating. The reaction mixture turned yellow and warmed up to 40-50°; the solids dissolved completely at first, then the whole mass crystallized. The mixture was left at room temperature for 16 hrs, after which there was added 15 ml of hot water. The crystalline product was filtered off after 3 hrs and was washed with water. M. p. 158° (from glacial acetic acid and from alcohol). The yield was 7.53 g (85%).

2-Phenyl-4-(o-carboxybenzyl-m,p-dimethoxybenzal)-5-oxazolone (II) is a yellow crystalline substance, sparingly soluble in water; its solubility in the majority of organic solvents is negligible.

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* For preparation of pure potassium salt of opianic acid, the commercial opianic acid was subjected to purification by method [6] and was neutralized with potassium carbonate.

Found %: C 70.35; H 4.76; N 3.32. $C_{26}H_{21}O_6N$. Calculated %: C 70.42; H 4.78; N 3.16.

Preparation of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid (III). 2-Phenyl-4-(o-carboxybenzyl-m,p-dimethoxybenzal)-5-oxazolone (4.43 g) was heated with 45 ml of 10% aqueous solution of potassium hydroxide in an apparatus for steam distillation. The hydrolysis was run with passage of steam into the apparatus, thus distilling the resulting benzyl alcohol. After termination of distillation of benzyl alcohol, the hydrolyzate was filtered and acidified with hydrochloric acid to Congo red. Upon this acidification there precipitated from the solution 7,8-dimethoxyisocarbostyryl-3-carboxylic and benzoic acids. Benzoic acid was steam distilled from this mixture (the presence of benzoic acid in the distillate was verified by a test with ferric chloride), while the 7,8-dimethoxyisocarbostyryl-3-carboxylic acid was filtered off. The yield was 2.44 g (98%); m. p. 261° (on Macquenne block) (from glacial acetic acid), which agreed with literature data [1].

Preparation of esters of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid (IV)-(VI). a) A mixture of 2.49 g of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid, 50 ml of anhydrous alcohol (methyl, ethyl or propyl) and 1.35 ml of sulfuric acid (d 1.84) was heated in a flask under a reflux condenser for 9 hrs on a boiling water bath. The resulting solution was poured into 150 g of a mixture of ice and water, containing 3 g of sodium carbonate. The ester which crystallized from the mixture was rapidly filtered off and washed with water until neutral to phenolphthalein. The filtrate was acidified with hydrochloric acid to Congo red and the precipitated 7,8-dimethoxyisocarbostyryl-3-carboxylic acid was filtered off. The yield of the methyl ester (IV) was 1.70 g (65%), m. p. 195° (from methyl alcohol) (m. p. 195° [1]). The yield of the ethyl ester (V) was 1.08 g (75%), m. p. 180° (from ethyl alcohol) (m. p. 179° [1]). The yield of the propyl ester (VI) was 2.25 g (77%), m. p. 146° (from propyl alcohol).

Found %: C 61.67; H 5.81; N 4.74. $C_{15}H_{17}O_5N$. Calculated %: C 61.84; H 5.88; N 4.81.

b) Preparation of butyl ester (VII). 7,8-Dimethoxyisocarbostyryl-3-carboxylic acid (2.49 g) was dissolved with heating in 200 ml of butyl alcohol. To the solution,cooled to 60-65°, there was added 1.2 ml of sulfuric acid (d 1.84) and the mixture was heated under a reflux condenser for 24 hrs at 60-65°. The resulting solution was washed with water, 2% solution of sodium carbonate and again with water until neutral to phenolphthalein. The washed solution of the butyl ester in butyl alcohol was then dried with anhydrous sodium sulfate, after which the butyl alcohol was distilled from it in vacuo. The yield was 1.86 g (64%); m. p. 128° (from butyl alcohol).

Found %: C 62.90; H 6.09; N 4.70. $C_{16}H_{19}O_5N$. Calculated %: C 62.94; H 6.27; N 4.59.

The esters of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid are colorless crystalline substances. The melting points in their series drop with increase in molecular weight. The esters are soluble in organic solvents, with the higher homologs being more soluble than the lower ones; the esters are practically insoluble in water. Alcoholic solutions of the esters give a green color with ferric chloride.

Cleavage of a methoxyl radical from 7,8-dimethoxyisocarbostyryl-3-carboxylic acid during its esterification with butyl alcohol. A mixture of 2.49 g of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid, 50 ml of butyl alcohol and 1.5 ml of sulfuric acid (d 1.84) was heated in a flask with a reflux condenser, provided with a calcium chloride tube, on a boiling water bath. The solution formed after heating the mixture for 8 hrs was left overnight in a refrigerator. The crystallized substance was filtered off and washed with butyl alcohol. The product was dissolved in 20 ml of acetone, the acetone solution was filtered and poured into 40 ml of a mixture of ice and water containing 0.3 g of sodium carbonate. The (VIII) ester which crystallized thereby was filtered off and washed with water until neutral to phenolphthalein. The yield was 1.23 g (42%); m. p. 168° (from toluene).

Butyl ester of (7?)-methoxy-(8?)-hydroxyisocarbostyryl-3-carboxylic acid (VIII) was a colorless crystalline substance, soluble in most organic solvents and practically insoluble in water. It gave a green color with ferric chloride. It reacts with phosphorus oxychloride, forming a product (not isolated in the pure state) which hydrolyzes very easily to the original butyl ester of methoxyhydroxyisocarbostyryl-3-carboxylic acid.

Found %: C 62.02; H 6.00; N 4.89. M 288; active H 1.97. $C_{15}H_{17}O_5N$. Calculated %: C 61.84; H 5.88; N 4.81; M 291; active H 2.

Decarboxylation of 7,8-dimethoxycarbostyryl-3-carboxylic acid was conducted by heating this acid on a salt bath at 270-300°. The heating was extended for 1 hr after which the mass was treated several times with 1% solution of potassium carbonate with heating. The undissolved residue was filtered off. 7,8-Dimethoxyisocarbostyryl was sublimated from the residue. The yield was 73%. M. p. 233°, corresponded to the literature data [1].

7,8-Dimethoxyisocarbostyryl (IX) is a colorless substance which is practically insoluble in the majority of organic solvents; it crystallizes well from dioxane. Its alcoholic solutions give a green color with ferric chloride.

All the experiments described above are well reproduced with larger amounts (for example, 10-15 fold) of the reagents.

SUMMARY

1. A method for the synthesis of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid was developed (using as the basis the method of Bain and co-workers) with the over-all yield of about 80%, calculated on the original potassium salt of opianic acid.

2. Four esters of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid, two of which (propyl and butyl), had not previously been described in the literature, were prepared in satisfactory yields.

3. It was shown that during the esterification of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid with butyl alcohol in the presence of sulfuric acid at a temperature about 100° there occurs the cleavage of one of the methoxyl groups at the isoquinoline ring.

4. A technique of preparative synthesis of 7,8-dimethoxyisocarbostyryl was developed.

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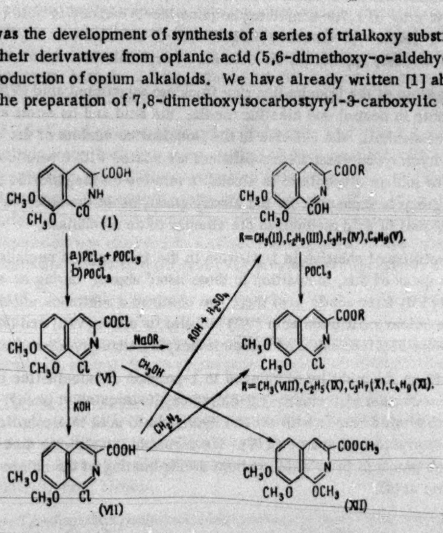
STUDIES IN THE FIELD OF ISOQUINOLINECARBOXYLIC ACIDS

II. PREPARATION OF 1-CHLORO SUBSTITUTED CARBOXYLIC ACID OF THE ISOQUINOLINE SERIES, ITS CHLORIDE AND ESTERS AND SOME DATA ON MOBILITY OF CHLORINE IN 1-POSITION OF THE ISOQUINOLINE NUCLEUS

L. I. Linevich

The goal of this study was the development of synthesis of a series of trialkoxy substituted acids of the isoquinoline group and some of their derivatives from opianic acid (5,6-dimethoxy-o-aldehydobenzoic acid), which is a waste product from the production of opium alkaloids. We have already written [1] about the first steps of the synthesis, which consisted of the preparation of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid (I) and its esters (II)-(V).



The problem in the present study consisted of the transformation of compounds of the isocarbostyryl series (I)-(V) into derivatives of 1-chloroisoquinoline (VI)-(XI), from which, by replacement of the chlorine atom by alkoxy groups, it is possible to prepare a series of trialkoxy substituted acids of the isoquinoline group and their derivatives,

We used phosphorus oxychloride and phosphorus pentachloride for the chlorinating agents. It turned out that the chlorination of derivatives of isocarbostyryl (I)-(V) proceeds under the same conditions, but that the rate of the reaction is noticeably affected by the substituent in position 3 of the isoquinoline ring. Chlorination of acid (I) was run in an organic solvent with a mixture of phosphorus pentachloride and oxychloride or by the action of excess phosphorus oxychloride. Under such conditions there takes place the formation of the chloride of 1-chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid (VI). This acyl chloride is notable for its stability in cold water and does not dissolve in a solution of sodium carbonate. The stability of this chloride in cold water is evidently the result of its insolubility in the latter. Literature data show, for example, a similar behavior in water of compounds close to it chemically, as for instance, the chloride of quinoline-4-carboxylic acid [2].

1-Chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid (VII) was prepared as the result of hydrolysis of its acyl chloride (VI) with caustic alkali. For characterization of the acid there was prepared from it by the action of diazomethane the corresponding methyl ester (VIII). The preparative synthesis of a series of esters of this acid was realized by: a) chlorination of corresponding esters of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid (II)-(V) and by b) action of equimolar amounts of sodium alcoholates dissolved in appropriate alcohols on the chloride of 1-chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid (VI). Thus were prepared methyl (VIII), ethyl (IX), propyl (X) and butyl (XI) esters of the chloro substituted acid. The first method of their preparation turned out to be the better one, since it assured higher yields of the esters.

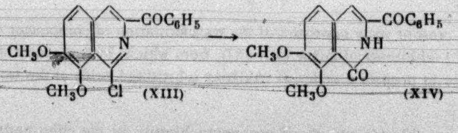
We failed to prepare these esters by heating the chloro substituted acid (VII) with excess of the alcohols in the presence of sulfuric or hydrochloric acids. It turned out that under these conditions the chlorine in 1-position of the isoquinoline nucleus is rather mobile and for this reason, along with the esterification of the carboxyl group, there occurs the substitution of the chlorine by a hydroxy group, owing to which there are formed esters of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid (II), (III). The source of the hydroxyl in this reaction is evidently the water formed in the esterification reaction.

A still greater increase of the mobility of chlorine in 1-position of the isoquinoline ring was observed in the attempt to prepare esters of the chloro substituted acid from its acyl chloride (VI) and an alcohol. During the reaction in the cold of the chloride of the chloro substituted acid (VI) with methyl alcohol there took place the formation of the methyl ester of 1,7,8-trimethoxyisoquinoline-3-carboxylic acid (XII). Thus, chlorine in 1-position of the chloride of 1-chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid (VI) by exchanging in the cold for an alkoxyl group of an alcohol, approaches the chlorine of acyl chlorides in reactivity.

Chlorine in 1-position of the isoquinoline ring in chloro substituted acid (VII), its chloride (VI) and esters (VIII)-(XI) is rather stable in neutral and alkaline media: the acid and its esters are not decomposed on being heated with dry and wet alcohols; the chlorine in the isoquinoline nucleus of the chloro substituted acid (VII) and its chloride (VI) is not hydrolyzed when these substances are heated with a solution of alkali; during the action of equimolar amounts of sodium alcoholates in alcoholic solution on the chloride (VI), only the chlorine atom bound to the carbonyl group is exchanged for the alkoxy group, while the chlorine of the isoquinoline nucleus is not exchanged as it happens in acid medium in the absence of an alcoholate.

The increased mobility of chlorine in 1-position in the isoquinoline nucleus occurs under the influence of acids. Following facts speak of this, in addition to those listed above: during an attempt to recrystallize the chloro substituted acid (VII) from acetic acid there was obtained a substance which did not contain chlorine; on heating of not only the chloro substituted acid (VII) but also its esters (VIII) and (IX) with alcohol in the presence of sulfuric acid there were obtained esters of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid (II) and (III).

The effect of acid on the mobility of halogen in 1-position of isoquinoline compounds was made apparent also in experiments on reduction of 1-chloro-7,8-dimethoxy-3-isoquinolyl phenyl ketone (XIII). In an attempt to reduce this chloro substituted ketone with tin and hydrochloric acid in alcoholic solution, there was obtained 7,8-dimethoxy-3-carbostyryl phenyl ketone (XIV). We succeeded in showing that its formation is the result of a hydrolytic process which proceeds in an acid medium during heating of the chloro substituted ketone (XIII) with alcohol and an inorganic acid.



The phenomenon of increase of halogen mobility in an acid medium in nitrogenous heterocyclic compounds was discovered in 1944 by Banks [3] in the example of the reaction of substitution of chlorine in triazines by the residues of substituted amines; this reaction has been studied but little [4, 5]. In the isoquinoline series this phenomenon has not been studied at all; only in 1951 there appeared a preliminary communication stating that 1-fluoroisoquinoline does not form a hydrochloride in dilute solutions and is easily hydrolyzed by dilute acid [6].

The increase of reactivity of chlorine in the isoquinoline compounds prepared by us, as displayed in acid medium, is explained by the fact that the nitrogen in these compounds, having a pair of free electrons, adds a proton in the acid medium and therefore obtains a positive charge; owing to this the shift of the electron cloud in the isoquinoline nucleus is increased in the direction of nitrogen. Here the electron density at carbon in 1-position is particularly decreased, since this is located in α-position in respect to the nitrogen. Therefore, a nucleophilic substitution proceeds in this location extremely readily.

Substituents in the nucleus, and specifically electronegative substituents (COCl, COOH, COOR, COC_6H_5) located in meta-position in respect to chlorine, should also act on the mobility of chlorine in the compounds prepared by us. The fact that the meta-located electronegative substituents do increase the activity of chlorine in an aromatic ring has been very convincingly shown by the work of V. N. Ufimtsev and M. M. Malafeeva [7]. The very high reactivity of chlorine in 1-position of isoquinoline derivatives prepared by us is evidently derived by the combination of the influence of nuclear nitrogen which increases in acid medium and the influence of the electronegative substituent in meta-position in respect to the chlorine atom.

EXPERIMENTAL

Preparation of the chloride of 1-chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid (VI). a) Into a round-bottomed flask provided with a reflux condenser with a calcium chloride tube there was placed 10 g of phosphorus pentachloride, 7.5 ml of phosphorus oxychloride and 200 ml of ethylene chloride dried over calcium chloride. Into the resulting solution there was added, in portions, 2.5 g of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid. The mixture was heated on a boiling water bath for 2.5 hrs, after which the solvent and phosphorus oxychloride were distilled in vacuo. The residue was recrystallized from toluene that had been distilled from sodium.

b) A mixture of 2.5 g of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid with 2.7 ml of phosphorus oxychloride was heated for 1 hr on a boiling water bath in a round-bottomed flask provided with a reflux condenser with a calcium chloride tube. After cooling, the mixture was treated with 100 g of ice and the crystallized product was filtered off and washed with water. The weight of the dry product was 2.8 g; m. p. 167°. If the resulting product is used for the preparation of 1-chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid (VII), there is no need to recrystallize it. No depression was observed in a mixed melting point of this substance with the chloride of 1-chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid (VI), prepared in experiment a).

The chloride of 1-chloro-7, 8-dimethoxyisoquinoline-3-carboxylic acid (VI) was obtained in the form of light yellow crystals; the substance was insoluble in cold water and in solutions of alkali carbonates; it was not decomposed by cold water, but was hydrolyzed by solutions of caustic alkalies; it was readily soluble in organic solvents (benzene, toluene, petroleum ether); it was decomposed by alcohols both on heating and in the cold.

Preparation of 1-chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid (VII). The chloride of 1-chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid (VI) (2.86 g) was dissolved with heating in 1% solution of potassium hydroxide. The resulting solution was filtered and to the filtrate there was added 10% sulfuric acid to acid test with Congo red; the crystallized 1-chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid (VI) was filtered off, washed with water and recrystallized from alcohol.

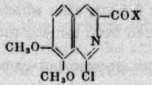
Methyl ester of 1-chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid (VIII) was prepared by the action of an ethereal solution of diazomethane on the solution of 0.1 g of the acid in 40 ml of methyl alcohol. (The methods of preparative synthesis of this ester are described below.) The residue after the distillation of excess diazomethane and solvents from the reaction mixture was dissolved in methyl alcohol, the solution was filtered and poured into a mixture of ice with an aqueous solution of sodium carbonate. The crystallized ester was filtered off, washed with water until neutral to phenolphthalein and recrystallized from methyl alcohol.

Preparation of esters of 1-chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid (VIII)-(XI). a) Chlorination of esters of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid (II)-(V). A mixture of 2.63 g of methyl ester of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid (or the equivalent amount of ethyl, propyl, or butyl ester) and 2.73 ml of phosphorus oxychloride was heated in a round-bottomed flask, provided with a reflux condenser with a calcium chloride tube, on a water bath for 2 hrs, after which the excess phosphorus oxychloride was distilled in vacuo. For purification of the methyl (VIII), ethyl (IX) and propyl (X) esters, the residue was washed with a small amount of the corresponding alcohol, dissolved with heating in the same alcohol; the solution was filtered and poured into 450 g of a mixture of ice with water containing 0.5 g of sodium carbonate. The crystallized ester was filtered off, washed with water until neutral to phenolphthalein and recrystallized from the corresponding alcohol. For purification of the butyl ester (XI), the residue after the distillation of phosphorus oxychloride was dissolved in dioxane and the dioxane solution was poured into a mixture of ice and water containing some sodium carbonate. The ester was recrystallized from butyl alcohol by freezing out.

b) Action of sodium alcoholate on the chloride of 1-chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid (VI). Metallic sodium (0.23 g) was dissolved in anhydrous alcohol (40 ml of methyl, ethyl, propyl or 8 ml of butyl) and the alcoholate solution was quantitatively transferred into a flask with 2.86 g of chloride of 1-chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid (VI). The reaction mixture was left overnight in a tightly closed flask. The resulting solution was poured into 200 g of ice (pH of the medium in the resulting mixture should be basic). The crystallized products (VIII)-(X) were rapidly filtered off and washed with ice water until neutral to phenolphthalein. In the preparation of the butyl ester (XI), the reaction mixture after completion of the reaction was diluted with 30 ml of dioxane and the resulting solution was poured into 250 g of mixture of ice and water. The separated ester was filtered off, washed with water until neutral to phenolphthalein and recrystallized from ethyl alcohol.

The corresponding esters (VIII)-(XI) prepared by the different methods melted at the same temperature (see table) and gave no depression in mixed melting points of appropriate specimens.

1-Chloro-7,8-dimethoxyisoquinoline-3-carboxylic Acid and Its Derivatives



No. of compound	X	Formula	M. p.	Yield (in %)	Elemental composition (in %)							
					found				calc.			
					C	H	N	Cl	C	H	N	Cl
(VI)	Cl	$C_{12}H_8O_3NCl_2$	168°	80; 85	50.40	3.19	4.95	24.50	50.37	3.17	4.90	24.78
(VII)	OH	$C_{12}H_{10}O_4NCl$	294 (on Macquenne block)	94	53.74	3.89	5.31	13.11	53.84	3.77	5.23	13.24
(VIII)	OCH_3	$C_{13}H_{12}O_4NCl$	166	72; 60	55.40	4.30	4.95	12.63	55.42	4.29	4.97	12.60
(IX)	OC_2H_5	$C_{14}H_{14}O_4NCl$	106	71; 55	56.79	4.76	4.84	11.96	56.86	4.77	4.73	11.99
(X)	OC_3H_7	$C_{15}H_{16}O_4NCl$	102	62; 60	57.99	5.24	4.66	11.41	58.16	5.21	4.52	11.45
(XI)	OC_4H_9	$C_{16}H_{18}O_4NCl$	77	80; 75	59.47	5.65	4.47	10.86	59.35	5.60	4.33	10.95

The four esters of 1-chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid prepared by us (methy, ethyl, propyl, and butyl) are colorless crystalline substances. The melting points in their series are lower for the higher homologs than for the lower ones. The esters are practically insoluble in water, but they are soluble in the majority of organic solvents, the solubility being greater among the higher homologs than the lower ones.

Hydrolysis of chlorine in 1-chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid and its esters in acid medium. a) A mixture of 0.27 g of 1-chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid (VII) or 0.28 g of its methyl ester (VIII), 5 ml of methyl alcohol and 0.15 ml of sulfuric acid (d 1.84) was heated on a boiling water bath for 6 hrs in a flask with a reflux condenser provided with a calcium chloride tube. The resulting solution was poured into 15 g of ice and water containing 0.3 g of sodium carbonate. The crystallized ester was filtered off, washed with water until neutral to phenolphthalein. The yield was 0.17 g (65%) of methyl ester of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid (II) with m. p. 195° (from alcohol) (m. p. 195° [8, 1]). The mixed melting point with methyl ester of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid prepared by us previously by another method [1] gave no depression.

b) From 0.27 g of 1-chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid (VII) or 0.29 g of its ethyl ester (IX), under the same conditions by replacement of methyl alcohol by ethyl alcohol there was obtained the ethyl ester of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid (III). Yield: 0.21 g (75%), m. p. 179°. Mixed melting point with ethyl ester of 7,8-dimethoxyisocarbostyryl-3-carboxylic acid prepared by us previously by another method [1] gave no depression.

Methanolysis of chloride of 1-chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid. A mixture of 2.86 g of the chloride of 1-chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid (VI) and 10 ml of anhydrous methyl alcohol was kept in a closed flask for 16 hrs at room temperature. The resulting solution was poured into 200 g of a mixture of ice and water containing 1.5 g of sodium carbonate. The separated crystals of methyl ester of 1,7,8-trimethoxyisoquinoline-3-carboxylic acid (XII) were filtered off and washed with water until neutral to phenolphthalein. M. p. 131° (from methyl alcohol). The ester did not contain active hydrogen. The Beilstein test and the test with ferric chloride were negative.

Found %: CH_3O 44.02; M 286. $C_{14}H_{15}O_5N$. Calculated %: CH_3O 44.72; M 277.

Hydrolysis of chlorine in 1-chloro-7,8-dimethoxyiso-3-quinolyl phenyl ketone (XIII) in acid medium. A mixture of 0.3 g of 1-chloro-7,8-dimethoxy-3-isoquinolyl phenyl ketone (XIII), 10 ml of methyl alcohol and 0.15 ml of sulfuric acid (d 1.84) was heated on a boiling water bath for 8 hrs in a flask with a reflux condenser. The mixture was cooled, the precipitate was filtered off, washed with alcohol, 2% solution of sodium carbonate and water until neutral to phenolphthalein. The yield was 0.15 g (50%) of 7,8-dimethoxy-3-isocarbostyryl phenyl ketone (XIV) with m. p. 199° (from alcohol) (m. p. 199° [9, 10]). The mixed melting point with 7,8-dimethoxy-3-isocarbostyryl phenyl ketone prepared by us by another method [9, 10] gave no depression.

SUMMARY

1. 1-Chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid and its chloride were prepared.

2. A series of esters of 1-chloro-7,8-dimethoxyisoquinoline-3-carboxylic acid (methyl,ethyl, propyl, and butyl) were prepared by two methods.

3. It was shown that the mobility of chlorine in 1-position in the isoquinoline nucleus in the above compounds shows an increase in acid medium and that this chlorine is readily subjected to hydrolysis and alcoholysis.

4. It was shown that chlorine in 1-chloro-7,8-dimethoxy-3-isoquinolyl phenyl ketone is readily hydrolyzed in acid medium.

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SYNTHESIS OF AMINO ACIDS OF ALIPHATIC SERIES FROM THIOPHENE DERIVATIVES

III. SYNTHESIS OF ω-AMINO ACIDS

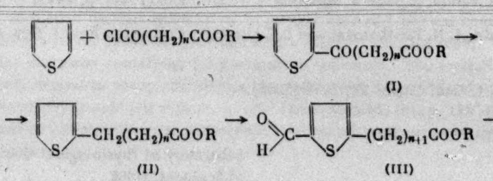
B. P. Fabrichnyi, I. F. Shalavina, and Ia. L. Gol'dfarb

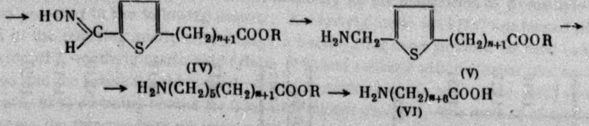
ω-Amino acids and the lactams formed by them have acquired a great significance in recent years mainly as the raw materials for the production of synthetic polyamide fibers. Owing to this, the interest shown by the investigators in studies of new methods of synthesis of amino acids of this type becomes understandable.

As it is known, one of the methods of preparation of lactams with 6-8 atoms of carbon is based on the use of the Beckmann rearrangement of oximes of the corresponding cyclic ketones, but this method is ill-suited for synthesis of lactams with a greater number of carbon atoms in the molecule since the starting ketones are difficult to obtain. The higher ω-amino acids are formed by the action of ammonia or potassium phthalimide on the corresponding ω-halogenated carboxylic acids [1, 2], by the cleavage of one molecule of water from diamides of dicarboxylic acids and by hydrogenation of the resulting amides of ω-cyanocarboxylic acids, as well as from aliphatic dinitriles by reduction of one nitrile group and hydrolysis of the resulting nitriles of ω-aminocarboxylic acids. Such methods do not always lead to the desired result and, for example, an attempt by M. N. Bogdanov [3] to prepare 7-aminoheptanoic acid from the dinitrile of pimelic acid ended in failure. In 1956 Treibs and Hauptmann [4] described a series of ω-amino acids prepared from monoamides of dicarboxylic acids by the Hoffmann method.

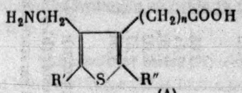
In light of the above-cited data, a special interest arises in the method of preparation of amino acids from the products of telomerization of ethylene and carbon tetrachloride, a method developed at the Institute of Heteroorganic Compounds of the Academy of Sciences, USSR [5]. It should be noted, however, that the necessity of utilization of a relatively complicated apparatus makes this method inconvenient at times under the laboratory conditions. Other methods [6, 7] have only a limited significance or are based on the utilization of natural substances. One may indicate also the data related to the preparation of mixtures of various amino acids [8]. ω-Amino acids with branched structure have been studied much less and they have been prepared mainly from oximes of the substituted cyclohexanones [9].

Thanks to the method of preparation of amino acids from thiophene derivatives, a method developed by us previously [10-12], the branched and the unbranched amino acids with even or odd number of atoms of carbon in the molecule have become readily accessible. Applied to ω-amino acids, this is shown in the series of examples illustrated in the following scheme:





This method was also used by us for the synthesis of 10-amino-3-methyldecanoic acid; the substituent which creates the branching of the carbon chain was introduced by acylation of thiophene with the chloride of β-methyl-γ-carbomethoxybutyric acid. The other possible starting materials for the preparation of aliphatic ω-amino acids with branched structure are the appropriate amino acids of the thiophene series with substituents in 3- or 4-positions of the thiophene nucleus as well as amino acids with the general formula (A), where R' and R" are atoms of hydrogen or hydrocarbon residues.


(A)

Esters of oxoacids with general formula (I), where R = CH_3 or C_2H_5, and n = 2, 3 or 4, were prepared by us by acylation of thiophene with the chlorides of β-carbomethoxypropionic, γ-carbomethoxybutyric, and δ-carboethoxyvaleric acids. The yields of esters of oxoacids reached 74-86%. The carbonyl group in the synthesized esters was reduced with hydrazine hydrate by a modified Kizhner method [13] (yield: 89-97%). Since the esters are hydrolyzed under these conditions, the reaction products in these cases were the acids with structure (II) (R = H). The latter were esterified prior to formylation (yield: 87-92%; this stage is not shown in the above scheme). The formylation of esters (II) was run with N-methylformanilide in the presence of phosphorus oxychloride (yield: 77-94%), while oximation of the resulting aldehyde-esters by heating with hydroxylamine gave yields above 90%. In some cases the resulting oximes could not be crystallized and these were used for the further reaction without purification. The reduction of oximino esters to esters of amino acids was done with amalgamated aluminum under conditions described previously [12]. The use of oximino esters instead of oximino acids at the reduction step permitted us to raise considerably the yield of the products and to bring this to 88% in the case of the ester of ε-(5-aminomethyl-2-thienyl)-hexanoic acid (V, R = CH_3, n = 4). In connection with the above, we shall note that the substitution for the reduction of the corresponding acetylhydrazones for the oximes of aldehyde-acids, as suggested by Decombe [14], failed to give satisfactory results. The corresponding amino acids were obtained from esters (V) by heating with a solution of barium hydroxide and neutralization with sulfuric acid. In some cases the resulting amino acids were not isolated as such, but were converted into the corresponding acetyl derivatives by the action of acetic anhydride in alkaline medium. This permitted us to raise the yield of the aliphatic amino acid since the hydrogenolysis of the acetyl derivatives proceeds with better yield than does the hydrogenolysis of esters of amino acids, reaching 83.5% for 9-acetamidononanoic acid; the hydrogenolysis was run by heating with Raney nickel in a dilute ammonia solution.

The hydrochlorides of the amino acids were obtained by heating the ω-acetamido acids with dilute hydrochloric acid; the melting points of the former agreed with the data cited in the literature.

By the above technique we were able to prepare the previously known 9-aminononanoic (VI, n = 2), 10-aminodecanoic (VI, n = 3), 11-aminoundecanoic (VI, n = 4) acids, while 10-amino-3-methyldecanoic acid is being described for the first time.

An attempt to prepare the ester of aliphatic ω-amino acid directly by hydrogenolysis of the oxime of aldehydo-ester (IV) without resorting to the intermediate step of reduction of the oxime to the ester of the amino acid (V) failed to give positive results in the case of 5-(3-carbethoxypropyl)-2-thiophenaldoxime.

EXPERIMENTAL

The esters of oxoacids of the thiophene series were synthesized by the action of chlorides of half-esters of dicarboxylic acids on thiophene in benzene medium in the presence of stannic chloride, using the previously described technique [15] into which the following changes were introduced: benzene was distilled from the solution of the condensation product and the residue was distilled in vacuo. The properties of the resulting esters of oxoacids are shown in Table 1.

TABLE 1

Esters of oxo acids	B. p. (pressure in mm)	d_4^{20}	n_D^{20}	Yield (in %)	Empirical formula	C (in %)		H (in %)		S (in %)	
						found	calc.	found	calc.	found	calc.
Methyl ester of β-(2-thenoyl)-propionic acid,[a] (I, n = 2)	174° (16)	—	1.5437	80	$C_9H_{10}O_3S$	—	—	—	—	—	—
Methyl ester of γ-(2-thenoyl)-butyric acid (I, n = 3)	173 (11)	1.1943	1.5377	74	$C_{10}H_{12}O_3S$	56.90, 56.87	56.58	5.78, 5.77	5.70	15.46, 14.92	15.10
Methyl ester of β-methyl-γ-(2-thenoyl)-butyric acid,[b] ($ThCOCH_2CH(CH_3)CH_2COOCH_3$)	173—174 (13)	1.1622	1.5320	86	$C_{11}H_{14}O_3S$	58.33, 58.50	58.38	6.27, 6.22	6.24	14.50, 14.30	14.17
Ethyl ester of δ-(2-thenoyl) valeric acid,[c] (I, n = 4)	185—186 (12)	1.1328	1.523	83	$C_{12}H_{16}O_3S$	60.02, 59.77	59.97	6.69, 6.65	6.71	13.42, 13.55	13.34

Note. a) Literature data [16]: b. p. 178° (17 mm), $n^{20}D$ 1.5428; b) Th – 2-thienyl; c) literature data [17]: b. p. 205° (20 mm), d_4^{25} 1.122, $n^{20}D$ 1.5152.

TABLE 2

Esters of oxo acids	B. p. (pressure in mm)	d_4^{20}	n_D^{20}	Yield (in %)	Empirical formula	C (in %)		H (in %)		S (in %)	
						found	calc.	found	calc.	found	calc.
γ-(2-Thienyl)-butyric acid,[a] (II, n = 2, R = H)	168° (14.5)	—	1.5317	90	$C_8H_{10}O_2S$						
Ethyl ester[b] (II, n = 2, R = C_2H_5)	143.5—144° (20)	1.0797	1.5020	92	$C_{10}H_{14}O_2S$	60.29, 60.39	60.57	6.97, 7.15	7.12	15.90, 16.09	16.17
δ-(2-Thienyl)-valeric acid[c] (II, n = 3, R = H)	177 (14) m.p. 41–43°	—	—	90	$C_9H_{12}O_2S$						
Methyl ester (II, n = 3, R = CH_3)	137.5—138 (14)	1.0620	1.5064	89	$C_{10}H_{14}O_2S$	60.71, 60.85	60.57	7.31, 7.15	7.12	16.05, 16.33	16.17
ε-(2-Thienyl)-caproic acid[d] (II, n = 4, R = H)	m.p. 41—41.5°	—	—	97	$C_{10}H_{14}O_2S$						
Methyl ester (II, n = 4, R = CH_3)	143.5—144 (12)	1.0636	1.5032	87	$C_{11}H_{16}O_2S$	62.28, 62.51	62.23	7.63, 7.74	7.60	15.31, 15.16	15.10
β-Methyl-δ-(2-thienyl)-valeric acid ($ThCH_2CH_2CH(CH_3)CH_2COOH$)[e]	172—173 (12)	1.1112	1.5212	89	$C_{10}H_{14}O_2S$	60.59, 60.83,	60.57	7.20, 7.03	7.12	16.23, 16.01	16.17
Methyl ester ($ThCH_2CH_2CH(CH_3)CH_2COOCH_3$)[e]	141.5—142 (14.5)	1.0641	1.5037	87	$C_{11}H_{16}O_2S$	62.42, 62.53	62.23	7.57, 7,54	7.60	14.94, 15.09	15.10

Note. a) Literature data [16, 20, 21]: b. p. 167° (14 mm), $n^{20}D$ 1.5321; b. p. 170-172° (14 mm), 130-134° (1.5 mm); b) $n^{23}D$ 1.5007, MR_D 54.16, calc. 53.97; ester number 287.3, calc. 282.4. Constants cited by Buu-Hoi and co-workers [23] for this ester (b. p. 164-65° at 20 mm, $n^{23}D$ 1.5081) did not agree with those found by us. c) Literature data [22]: b. p. 178° (14 mm), m. p. 36°; d) literature data [17]: m. p. 40°; e) Th – 2-thienyl.

β-Methyl-γ-carbomethoxybutyryl chloride, necessary for the preparation of β-methyl-γ-(2-thenoyl)-butyric acid, was prepared in the following manner. β-Methylglutaric acid [18] was heated with acetic anhydride with distillation of the resulting acetic acid through a fractionating head provided for total condensation. The resulting anhydride of β-methylglutaric acid (yield: 81%) was refluxed with methanol, the excess methanol was distilled in vacuo and the residual acid methyl ester of β-methylglutaric acid (yield: 80%) yielded the corresponding chloride (yield: 95%) on being heated for 2 hrs with thionyl chloride. The method of synthesis used by us permitted us to prepare the intermediate substances and the chloride in better yields than under previously described conditions [19].

Acids (II) were prepared by reduction of the esters of oxoacids shown in Table 1, by the Kizhner method as modified by Huang-Minlon [13]. The esters of these acids were prepared by heating the acid with a saturated solution of hydrogen chloride in the appropriate alcohol. The constants of the acids and their esters are shown in Table 2.

The resulting esters (II) were converted into the corresponding substituted 2-thiophenaldehydes by the action of N-methylformanilide in the presence of phosphorus oxychloride [24]. The oximes of the substituted 2-thiophenaldehydes were prepared by the action of a slight excess of hydroxylamine on the appropriate aldehydes in dilute alcohol.

5-(γ-Carbethoxypropyl)-2-thiophenaldoxime. To a solution of hydroxylamine (from 6.95 g of hydroxylamine hydrochloride in 15 ml of water and 5.3 g of sodium carbonate in 15 ml of water) there was added 22.6 g of 5-(γ-carbethoxypropyl)-2-thiophenaldehyde, followed by alcohol until a transparent solution formed. This was refluxed for 1 hr. To the cooled solution there was added enough water to give a stable turbidity, and on cooling of the solution a colorless oil separated, which was then extracted with ether. After distillation of ether there was obtained 22.3 g (91.7%) of an oily oxime which could not be crystallized. For cleavage of the ester group, the compound was hydrolyzed by heating with dilute alkali. Acidification with hydrochloric acid yielded the oxime of 5-(γ-carboxypropyl)-2-thiophenaldehyde, which melted with decomposition at 182-184° (from dilute methanol).

Found %: C 50.92, 50.65; H 5.29, 5.18; S 14.78, 14.98. $C_9H_{11}O_3NS$. Calculated %: C 50.69; H 5.20; S 15.03.

Oximes of 5-(δ-carbomethoxybutyl)-2-thiophenaldehyde and 5-(ε-carbomethoxypentyl)-2-thiophenaldehyde were prepared as indicated above. The oxime of 5-(γ-methyl-δ-carbomethoxybutyl)-2-thiophenaldehyde was obtained in 97% yield in the form of a yellow oil. The constants of the aldehydes prepared by us, and of their oximes and other derivatives are shown in Table 3 (melting points are given for substances recrystallized from dilute alcohol).

γ-(5-Aminomethyl-2-thienyl)-butyric acid. The solution of 13.3 g of the oxime of 5-(γ-carbethoxypropyl)-2-thiophenaldehyde in a mixture of 105 ml of alcohol and 100 ml of water was added to amalgamated aluminum [25] prepared from 20 g of aluminum in granular form. The mixture was shaken for 30 hrs. The aluminum hydroxide was filtered off and washed repeatedly with alcohol. The filtrates were combined, the alcohol and part of the water were distilled in vacuo and the residue was extracted with ether. The extract was dried with magnesium sulfate and the ether was distilled. There remained 8.5 g (67.8%) of ethyl ester of γ-(5-aminomethyl-2-thienyl)-butyric acid in the form of a yellow oil. The hydrochloride of this ester, prepared by passage of dry hydrogen chloride into an ethereal solution of the ethyl ester of the amino acid, had m. p. 148-149° (from a mixture of absolute isopropyl alcohol and acetone).

Found %: C 50.02, 50.02; H 6.92, 6.89; Cl^- 13.11, 13.20. $C_{11}H_{18}O_2NClS$. Calculated %: C 50.08; H 6.88; Cl^- 13.44.

Picrate of ethyl ester of the amino acid, prepared by addition of an aqueous solution of picric acid to an aqueous solution of the hydrochloride, had m. p. 106-107° (from dilute alcohol).

Found %: C 44.99, 44.91; H 4.36, 4.40; S 7.21, 7.02. $C_{17}H_{20}O_9N_4S$. Calculated %: C 44.73; H 4.42; S 7.03.

The hydrochloride of γ-(5-aminomethyl-2-thienyl)-butyric acid was prepared by heating the ester of the amino acid with dilute hydrochloric acid followed by evaporation of the solution; the product, after reprecipitation with ether from a solution in isopropyl alcohol, had m. p. 166-167° (with decomposition).

TABLE 3

Aldehydes and their derivatives	B. p. (pressure in mm)	M. p.	Yield (in %)	Empirical formula	C (in %)		H (in %)		N (in %)		S (in %)	
					found	calc.	found	calc.	found	calc.	found	calc.
5-(γ-Carbethoxypropyl)-2-thiophenaldehyde (III, n = 2)*	187° (13)	—	83	$C_{11}H_{14}O_3S$	58.37, 58.57	58.38	6.21, 6.27	6.24	—	—	—	—
Semicarbazone	—	163.5—165°	—	$C_{12}H_{17}O_3N_3S$	—	—	—	—	14.68, 14.94	14.83	—	—
Acetylhydrazone	—	99—100	—	$C_{13}H_{18}O_3N_2S$	55.32, 55.10	55.29	6.62 6.55	6.43	—	—	11.28, 11.13	11.36
5-(δ-Carbomethoxybutyl)-2-thiophenaldehyde (III, n = 3)	163—165 (1.5)	66—67	94	$C_{11}H_{14}O_3S$	58.27, 58.41	58.38	6.17, 6.26	6.24	—	—	14.11, 14.30	14.17
Oxime	—	54—55	97	$C_{11}H_{15}O_3NS$	54.70, 54.53	54.75	6.28, 6.19	6.27	—	—	13.10, 13.20	13.29
Semicarbazone	—	165	—	$C_{12}H_{17}O_3N_3S$	—	—	—	—	14.87, 14.86	14.83	—	—
5-(ε-Carbomethoxypentyl)-2-thiophenaldehyde (III, n = 4)	195—197 (13)	36—37	77	$C_{12}H_{16}O_3S$	59.76, 59.68	59.97	6.61, 6.61	6.71	—	—	13.49, 13.42	13.34
Oxime	—	62—63	95	$C_{12}H_{17}O_3NS$	56.10, 56.27	56.44	6.59, 6.70	6.71	—	—	12.56, 12.75	12.56
Semicarbazone	—	159—160	—	$C_{13}H_{19}O_3N_3S$	52.67, 52.43	52.50	6.35, 6.41	6.44	—	—	10.96, 11.07	10.78
5-(γ-Methyl-δ-carbomethoxybutyl)-2-thiophenaldehyde** $(T-CH_2CH_2CH(CH_3)CH_2COOCH_3)$***	160 (2)	—	84	$C_{12}H_{16}O_3S$	60.34, 60.21	59.97	6.74, 6.83	6.71	—	—	13.13, 12.90	13.34
Semicarbazone		167—168	—	$C_{13}H_{19}O_3N_3S$	—	—	—	—	14.37, 14.19	14.13	—	—

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* $n^{20}D$ 1.5371.

** d_4^{20} 1.1320, $n^{20}D$ 1.5362.

*** T − 2-formyl-5-thienyl.

Found %: C 46.23, 46.36; H 6.18, 6.10; Cl^- 14.70, 14.78. $C_9H_{14}O_2NClS$. Calculated %: C 45.86; H 5.99; Cl^- 15.04.

γ-(5-Aminomethyl-2-thienyl)-butyric acid, melting with decomposition at 213-214° (from dilute acetone), was obtained by the action of silver oxide on the above hydrochloride.

Found %: C 54.17, 54.11; H 6.61, 6.66; S 16.20, 15.91. $C_9H_{13}O_2NS$. Calculated %: C 54.24; H 6.58; S 16.09.

δ-(5-Aminomethyl-2-thienyl)-valeric acid. A solution of 20.0 g of oxime of 5-(δ-carbomethoxybutyl)-2-thiophenaldehyde in 300 ml of methanol and 150 ml of water was shaken for about 40 hrs with amalgamated aluminum (from 20 g of granular aluminum). Working up of the reaction mixture gave 15.2 g of methyl ester of δ-(5-aminomethyl-2-thienyl)-valeric acid in the form of a red-brown oil (yield 80.7%). The ester was heated for 4 hrs with a solution of 18.6 g of crystalline barium hydroxide in 100 ml of water and the resulting solution was diluted with 200 ml of water and exactly neutralized with dilute sulfuric acid. The precipitate was filtered off and repeatedly washed with boiling water. By evaporation of the filtrates there was obtained 9.18 g (yield: 52%, calculated on the oxime) of the amino acid with m. p. 182-186°. After washing with alcohol and ether and recrystallization from water, the amino acid had m. p. 201-202° (with decomposition).

Found %: N 6.63, 6.56. $C_{10}H_{15}O_2NS$. Calculated %: N 6.59.

The hydrochloride of δ-(5-aminomethyl-2-thienyl)-valeric acid was prepared by treatment of the amino acid with dilute hydrochloric acid and evaporation of the solution in vacuo; the product had m. p. 156-157.5° (from isopropyl alcohol).

Found %: C 47.94, 47.84; H 6.48, 6.53; N 5.71, 5.83; Cl^- 14.10, 14.01. $C_{10}H_{16}O_2NClS$. Calculated %: C 48.09; H 6.46; N 5.61; Cl^- 14.20.

ε-(5-Aminomethyl-2-thienyl)-caproic acid was prepared by the reduction of the oxime of 5-(ε-carbomethoxypentyl)-2-thiophenaldehyde with amalgamated aluminum and hydrolysis of the resulting methyl ester of the amino acid by heating it with a solution of barium hydroxide. The yield was 69.6% (based on oxime). After purification the amino acid melted with decomposition at 185-186° (from water).

Found %: C 57.99, 57.87; H 7.45, 7.34; N 6.04, 6.01; S 13.97, 13.78. $C_{11}H_{17}O_2NS$. Calcuated %: C 58.12; H 7.54; N 6.16; S 14.11.

The hydrochloride of this amino acid had m. p. 143-144.5° (from isopropyl alcohol).

Found %: N 5.45, 5.41; Cl^- 13.24, 13.42. $C_{11}H_{18}O_2NClS$. Calculated %: N 5.31; Cl^- 13.44.

β-Methyl-δ-(5-aminomethyl-2-thienyl)-valeric acid. From 24 g of oily oxime of 5-(γ-methyl-δ-carbomethoxybutyl)-2-thiophenaldehyde there was prepared by the above-described method 20.3 g (89.5%) of unpurified methyl ester of β-methyl-δ-(5-aminomethyl-2-thienyl)-valeric acid in the form of a light yellow oil. By hydrolysis of this ester by heating with a solution of barium hydroxide there was obtained 16.7 g of crude amino acid (yield: 78%, based on the oxime). After recrystallization from dilute acetone, the amino acid melted with decomposition at 196-198°.

Found %: C 57.87, 57.82; H 7.53, 7.60; N 6.30, 6.08; S 13.98, 13.94. $C_{11}H_{17}O_2NS$. Calculated %: C 58.12; H 7.54; N 6.16; S 14.11.

The hydrochloride of this amino acid, after reprecipitation from a solution in anhydrous isopropyl alcohol with ether, had m. p. 151-152°.

Found %: C 50.04, 49.87; H 6.88, 6.80; Cl^- 13.19, 13.29. $C_{11}H_{18}O_2NClS$. Calculated %: C 50.08; H 6.88; Cl^- 13.44.

γ-(5-Acetamidomethyl-2-thienyl)-butyric acid. There was prepared 16.7 g of ethyl ester of γ-(5-aminomethyl-2-thienyl)-butyric acid by the reduction of 25.0 g of the oxime of 5-(γ-carbethoxypropyl)-2-thiophenaldehyde in 400 ml of alcohol and 250 ml of water by amalgamated aluminum (from 37.5 g of aluminum in granular form); the ester without further purification was heated for 4 hrs with 5.9 g of sodium hydroxide in 50 ml of water. The solution was evaporated to dryness in vacuo and to the residue, dissolved in 50 ml of water, there was added gradually 10 ml of acetic anhydride with ice cooling and stirring. After 1 hr the small amount of separated and was brought into solution by addition of sodium hydroxide solution. After acidification with hydrochloric acid there precipitated a rapidly crystallizing oil. After washing with cold water and drying there was obtained 14.7 g of the acetamido acid (yield: 59% based on the oxime); m. p. 95-96° (from water).

Found %: C 54.70, 54.70; H 6.26, 6.27; S 13.46, 13.30. $C_{11}H_{15}O_3NS$. Calculated %: C 54.75; H 6.27; S 13.29.

δ-(5-Acetamidomethyl-2-thienyl)-valeric acid. From 14.6 g of oxime of 5-(δ-carbomethoxybutyl)-2-thiophenaldehyde there was prepared, by the above-cited method, 9.1 g (59% based on the oxime) of the acetamido acid; m. p. 80-81.5° (from water).

Found %: C 56.20, 56.34; H 6.64, 6.63; S 12.52, 12.62. $C_{12}H_{17}O_3NS$. Calculated %: C 56.45; H 6.71; S 12.56.

ε-(5-Acetamidomethyl-2-thienyl)-caproic acid was prepared by reduction of the oxime of 5-(ε-carbomethoxypentyl)-2-thiophenaldehyde with amalgamated aluminum, hydrolysis of the resulting methyl ester of ε-(5-aminomethyl-2-thienyl)-caproic acid with a sodium hydroxide solution and acetylation of the amino acid with acetic anhydride. The yield was 84% based on the oxime. After repeated recrystallization from water, the acetamido acid had m. p. 93-94°.

Found %: C 57.50, 57.70; H 7.02, 7.06; S 12.01, 11.98. $C_{13}H_{19}O_3NS$. Calculated %: C 57.96; H 7.11; S 11.91.

β-Methyl-δ-(5-acetamidomethyl-2-thienyl)-valeric acid was obtained in the form of an oil from the oxime of 5-(γ-methyl-δ-carbomethoxybutyl)-2-thiophenaldehyde by the above-described method in a yield of 72.5%, based on the oxime. The crystalline acetamido acid was obtained by acetylation of the purified β-methyl-δ-(5-aminomethyl-2-thienyl)-valeric acid with acetic anhydride; m. p. 64-65° (from dilute alcohol).

Found %: C 57.87, 58.09; H 7.02, 6.93; S 11.87, 11.90. $C_{13}H_{19}O_3NS$. Calculated %: C 57.96; H 7.11; S 11.91.

9-Acetamidononanoic acid. γ-(5-Acetamidomethyl-2-thienyl)-butyric acid (5.5 g) was dissolved in 200 ml of water and 30 ml of concentrated ammonia, the solution was heated to 65° and treated with about 33 g of Raney nickel with stirring. The mixture was stirred at 70-75° for 5 hrs (until the sulfur test vanished). The nickel was filtered off and washed with hot water. The combined filtrates were evaporated to dryness in vacuo on a water bath and the residue was dissolved in 50 ml of hot water and filtered from aluminum hydroxide. The filtrate, cooled with ice, was acidified to Congo red with dilute hydrochloric acid. The resulting precipitated crystals were filtered off and washed with cold water. There was obtained 4.1 g (83.5%) of crude acetamido acid with m. p. 68-72°. The pure substance melted at 71-72° (from dilute alcohol).

Found %: C 61.28, 61.24; H 9.80, 9.74. $C_{11}H_{21}O_3N$. Calculated %: C 61.36; H 9.83.

A mixed melting point of this substance with a specimen of 9-acetamidononanoic acid prepared by us * was 71-72°.

Hydrochloride of 9-aminononanoic acid was prepared from 4.6 g of 9-acetamidononanoic acid by refluxing for 10 hrs with dilute (1:1) hydrochloric acid. The filtrate was evaporated to dryness in vacuo and the residue was dried over phosphoric anhydride. The crude hydrochloride (4.4 g) melted at 122-125°. After recrystallization from a mixture of anhydrous isopropyl alcohol and acetone it had m. p. 132-133°. Literature data [27, 28, 4, 1]: m. p. 115°, 115-118°, 128-129°, and 130-133°.

9-Aminononanoic acid was isolated from the solution of its hydrochloride by addition of the calculated amount of sodium carbonate; m. p. 185-186° (from water). Literature data [2, 4]: m. p. 177° and 186-187°. A mixed melting point with an authentic specimen of 9-aminononanoic acid gave no depression.

10-Acetamidodecanoic acid. From 5.4 g of δ-(5-acetamidomethyl-2-thienyl)-valeric acid, after heating with 24 g of Raney nickel, there was obtained 3.5 g (72%) of crude acetamido acid with m. p. 118.5-120°. The pure substance melted at 120-121° (from dilute alcohol).

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* The speciment of 9-acetamidononanoic acid was prepared from 9-aminononanoic acid obtained from R. Kh. Freidlina. Earlier, 9-acetamidononanoic acid had not been obtained in the pure state; Middleton and Barrett [26] had prepared it in a mixture with monomethylamide of sebacic acid; the mixture had m. p. 65-72°.

Found %: C 62.47, 62.47; H 10.01, 10.08; N 6.22, 6.10. $C_{12}H_{23}O_3N$. Calculated %: C 62.85; H 10.11; N 6.11.

Hydrochloride of 10-aminodecanoic acid. By heating 2.23 g of the corresponding acetamido acid with dilute hydrochloric acid for 10 hrs there was obtained 2.0 g of crude hydrochloride. The pure hydrochloride melted at 157-159° (from a mixture of anhydrous isopropyl alcohol and acetone).

Found %: N 6.46, 6.37; Cl^- 15.48, 15.61. $C_{10}H_{22}O_2NCl$. Calculated %: N 6.26; Cl^- 15.84.

10-Aminodecanoic acid was isolated from the solution of its hydrochloride by means of sodium carbonate; m. p. 185-187° (from water). Literature data [1]: m. p. 185-186°.

Found %: C 63.56, 63.51; H 11.28, 11.17; N 7.51, 7.70. $C_{10}H_{21}O_2N$. Calculated %: C 64.13; H 11.30; N 7.48.

11-Acetamidoundecanoic acid. From 5.0 g of ϵ-(5-acetamidomethyl-2-thienyl)-caproic acid with m. p. 89-90° there was obtained, by the action of 40 g of Raney nickel, 2.95 g (65%) of crude acetamido acid with m. p. 81-83°. After recrystallization from dilute alcohol, m. p. 83-84°.

Found %: C 63.96, 63.74; H 10.25, 10.28. $C_{13}H_{25}O_3N$. Calculated %: C 64.16; H 10.35.

Hydrochloride of 11-aminoundecanoic acid. By hydrolysis of 1.73 g of 11-acetamidoundecanoic acid with dilute hydrochloric acid 1.72 g of crude hydrochloride with m. p. 142-144°. The pure substance had m. p. 144-145° (from a mixture of isopropyl alcohol and acetone).

Found %: N 5.89, 5.87; Cl^- 14.47, 14.67. $C_{11}H_{24}O_2NCl$. Calculated %: N 5.89; Cl^- 14.91.

11-Aminoundecanoic acid was isolated from an aqueous solution of its hydrochloride by addition of sodium carbonate. M. p. 184-186° (from water). Literature data [1]: m. p. 186-187°.

Found %: C 65.77, 65.65; H 11.44, 11.35; N 7.07, 6.98. $C_{11}H_{23}O_2N$. Calculated %: C 65.63; H 11.51; N 6.96.

10-Acetamido-3-methyldecanoic acid. By the action of 100 g of Raney nickel on a solution of 14.3 g of the oily β-methyl-δ-(5-acetamidomethyl-2-thienyl)-valeric acid in 350 ml of water and 50 ml of concentrated ammonia, with the subsequent work-up, there was obtained 8.1 g (62.4%) of crude acetamido acid with m. p. 68-72°. The pure substance had m. p. 74-75° (from dilute alcohol).

Found %: C 63.92, 63.77; H 10.19, 10.20; N 6.05, 6.15. $C_{13}H_{25}O_3N$. Calculated %: C 64.16; H 10.35; N 5.76.

Hydrochloride of 10-amino-3-methyldecanoic acid. There was obtained 2.7 g of crude hydrochloride by heating 3.0 g of crude acetamido acid with 30 ml of dilute hydrochloric acid. After three recrystallizations from a mixture of isopropyl alcohol and ether there was obtained 1.15 g of the pure hydrochloride with m. p. 83-84°. This hydrochloride was readily soluble in water and alcohol.

Found %: C 55.58, 55.81; H 9.82, 9.99; Cl^- 15.06, 14.66. $C_{11}H_{24}O_2NCl$. Calculated %: C 55.56; H 10.17; Cl^- 14.91.

10-Amino-3-methyldecanoic acid was isolated from its hydrochloride (2.38 g) by the action of silver oxide. There was obtained 1.53 g of the amino acid with m. p. 174-175.5°. The pure amino acid melted at 178-179° (from alcohol) with decomposition. It was readily soluble in cold water.

Found %: C 65.10, 64.82; H 11.34, 11.37; N 6.81, 6.99. $C_{11}H_{23}O_2N$. Calculated %: C 65.63; H 11.51; N 6.96.

SUMMARY

1. It was shown that the previous suggested method of synthesis of aliphatic amino acids from compounds of the thiophene series may be used for the preparation of aliphatic ω-amino acids with normal and branched structures.

2. By reduction of oximes of appropriate aldehyde esters of the thiophene series there were prepared esters of γ-(5-aminomethyl-2-thienyl)-butyric, δ-(5-aminomethyl-2-thienyl)-valeric, ε-(5-aminomethyl-2-thienyl)-caproic, and β-methyl-δ-(5-aminomethyl-2-thienyl)-valeric acids.

3. By hydrogenolysis of the acetyl derivatives of the above-listed amino acids of the thiophene series there were prepared: 9-acetamidononanoic, 10-acetamidodecanoic, 11-acetamidoundecanoic and 10-acetamido-3-methyldecanoic acids and from these were prepared, by a subsequent treatment, the corresponding amino acids and their hydrochlorides.

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SYNTHESIS OF SOME ADRENALINE DERIVATIVES

I. SYNTHESIS OF D,L-ADRENALINE AND ITS ANALOGS

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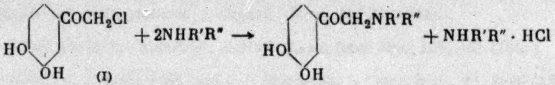
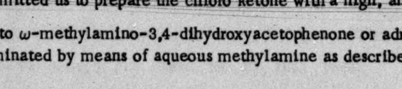
The synthesis of some adrenaline derivatives described in this paper were undertaken with the purpose of studying their anti-inflammatory properties. Although the majority of the compounds considered below have been known for a long time, their synthesis remained rather poorly developed and the published directions often contained inaccuracies and could not be always reproduced. Therefore the additional data obtained by us and presented in this paper have a certain significance insofar as they touch upon compounds which play an extremely important role in the physiological studies.

In the scheme proposed at one time by Stolz [1] and used by us in the present work, the synthesis of adrenaline and its analogs includes the following two steps:

1) Amination of ω-chloro-3,4-dihydroxyacetophenone (I) with its transformation, depending on the amine used for the reaction, into the corresponding amino ketone:



and 2) reduction of the resulting amino ketone to the corresponding secondary alcohol – D,L-adrenaline (IV) or its analog:

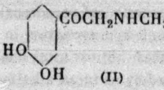


In the preparation of ω-chloro-3,4-dihydroxyacetophenone (I), which is the starting material in the synthesis being discussed here, we tested three known methods[2-5] among which the preference was given to the method of Schlotta and Heller [5] in which pyrocatechol is condensed with chloroacetyl chloride. After introduction of minor changes, this method permitted us to prepare the chloro ketone with a high, and reproducible, yield.

For its transformation into ω-methylamino-3,4-dihydroxyacetophenone or adrenalone (II), the dihydroxychloroacetophenone (I) was aminated by means of aqueous methylamine as described by Stolz [1] and Dakin [3] without any complications.

The ω-amino-3,4-dihydroxyacetophenone – so-called noradrenalone (III) – was prepared analogously to the preparation of adrenalone. The data in the existing literature bearing on amination of dihydroxychloroacetophenone (I) with ammonia, are very brief [6]. In reproducing the directions of Stolz [1] it turned out that the process in this case proceeds less smoothly than in the preparation of adrenalone, this fact being in part connected with the concurrent intense oxidation of the reaction product. Considering this, we ran the amination under complete exclusion of air in an ammonia atmosphere, which modification raised the yield noticeably and improved the quality of the resulting noradrenalone.

Reduction of adrenalone had been until recently the most complex step in the synthesis of racemic adrenaline (IV). The best method for its realization is unquestionably the method of catalytic hydrogenation. Palladium has usually been used for the catalyst and the reaction was run in hydrochloric acid solution since the adrenalone base is practically insoluble in either water or alcohol. The conditions of hydrogenation were explored in detail in [7]. Hydrogenation of adrenalone in an alkaline solution over Raney nickel has been described also [8]. In the last paper, which had an exploratory character, the optimum reaction conditions were not fixed exactly. However, by using the data given in this paper we were able to select the conditions under which the yield of the product of hydrogenation reached 95% in individual experiments and usually was 88-90%. Thus, this step in the adrenaline synthesis may be considered at this time to be the most simple and dependable one. Hydrogenation of noradrenalone (III) to racemic α-aminomethyl-3,4-dihydroxybenzyl alcohol (V), the so-called noradrenaline or arterenol, was also run in an alkaline medium with nickel catalyst. In this case as well the reaction proceeded well and rapidly.*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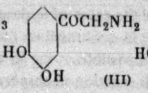
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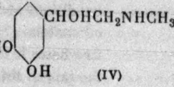
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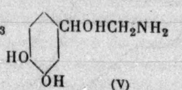
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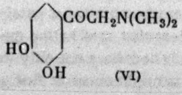
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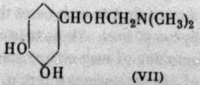
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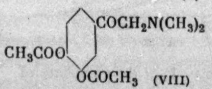
(VIII)

A special interest lies in the synthesis of N-methyladrenalone (VI) and D,L-N-methyladrenaline (VII). These substances, so close to the structure of noradrenalone and adrenalone and, respectively, noradrenaline and adrenaline, differ from these in physiological activity in the most radical fashion: amino ketone (VI) shows no adrenaline-like physiological activity, while amino alcohol (VII) possesses it only to a small degree [9]. They also differ in the physicochemical properties. As it is known, the bases of adrenalone and adrenaline (as well as noradrenalone and noradrenaline) do not dissolve in water and other neutral solvents and are easily isolated from the salts in the form of crystalline bases by simple addition of alkali. Their N-methyl derivatives, on the contrary, are considerably soluble in water and alcohols. Among them we succeeded in isolating only N-methyladrenalone (VI) in the form of amorphous base (until this time it was known only in the form of salts). As to the base of racemic N-methyladrenaline (VII) it was so soluble and separated from solutions so poorly that we failed to obtain it in the solid state. The absence of certain methods of preparation of N-methyladrenaline or, as it is called, metadrine, in the crystalline form forced biologists to work with specimens whose chemical individuality could be taken under much doubt. Therefore, it was important to find a method of preparation of this interesting compound in the crystalline state. After unsuccessful attempts to use the already published dubious patent data related to the base [10, 11], and the directions for preparation of metadrine hydrochloride [12] which could not be obtained in the crystalline state, we developed the conditions for its preparation with isolation of the product in the form of a stable and readily crystallizing phosphate. The raw material, as in the previous experiments, was ω-chloro-3,4-dihydroxyacetophenone (I). The amination of this substance with dimethylamine, first was accomplished by S. K. Dzerzhgovskii [13] who isolated the resulting N-methyladrenalone in the form of oxalate salt which by exchange reaction with calcium chloride was transformed by him into the hydrochloride.

The directions of Dzerzhgovskii were refined by us and simplified considerably. It appeared that the oxalate prepared by that author and having m. p. 235° was not the hydrogen oxalate but the neutral salt. It also appeared that the almost completely pure hydrochloride of N-methyladrenalone may be isolated directly from the reaction mixture in 75% yield if the excess dimethylamine is preliminarily distilled off in vacuo.

It was shown that this salt exists in the form of two crystalline modifications with m. p. 236° and 212°,** the second of which had been unknown until now despite the fact that it is the more common one, although the less stable one.

Since the amorphous free base of N-methyladrenalone, isolated from the hydrochloride by us and undescribed in previous literature, could not be obtained in an analytically pure state, it was transformed for the proof of structure and for analysis into the diacetyl derivative (VIII) which was prepared and analyzed in the form of the base, hydrochloride and picrate.

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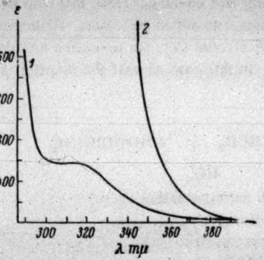
* We were the first to prepare noradrenaline under these conditions.

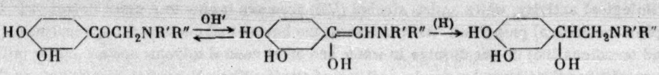
** Here as in the following exposition the temperature given is corrected for the exposure of the mercury column.

N-Methyladrenalone could be hydrogenated in the form of the base in methanolic solution with palladium precipitated on carbon, which fact had a considerable significance from the preparative viewpoint since it considerably simplified the isolation of the hydrogenation product in the pure state. The reaction was run at room temperature with a slight excess pressure (0.2 atmos) and required 48 hrs. Upon replacement of the palladium catalyst by Raney nickel, the hydrogenation practically failed to proceed at all under these conditions, but if one added alkali to the alcoholic solution of the ketone which was being reduced, the absorption of hydrogen proceeded rapidly and quantitatively and was completely finished in 3 hrs.



Absorption spectra: 1) of the phosphate of N-methyladrenaline, 2) of the phosphate of N-methyladrenalone.

Comparison of the data, known from the literature, about the conditions and the rates of hydrogenation of noradrenalone [6] and adrenalone [7] in acid medium (their hydrogenation in the form of free bases is impossible owing to their almost total insolubility) with the rate of this reaction as observed by us in an alkaline medium showed that in such cases there is exhibited a catalytic action of the hydroxyl ions. Thus, it is clear that an alkaline medium in hydrogenation of such compounds is necessary not only for the formation of a homogeneous solution, as might occur at first glance, but also plays an independently important role. One may allow with a considerable measure of probability that the catalytic role of hydroxyl ions is connected with the displacement of keto-enol tautomeric equilibrium toward the enolic form of the amino ketone, which is then hydrogenated at the double bond.



There are indications in the literature about the catalytic effect of alkali in hydrogenation of some other ketones [14].

Attempts to isolate the free base of the reaction product from the reaction mixture, obtained after hydrogenation of N-methyladrenalone, were unsuccessful. The tarry residue obtained after the removal of the solvent oxidized rapidly in air and could not be purified. However, after neutralization of it with phosphoric acid in anhydrous ethanol there was obtained in 80% yield a quite stable and readily crystallizable monosubstituted phosphate. It separated from the solution almost without loss and therefore the magnitude of the yield did not correspond to the quantitatively run hydrogenation. It was supposed that one of the reasons for the lowering of the yield may be deamination which accompanies the hydrogenation of N-methyladrenalone analogously to the previous observation of hydrogenation of some other similar amino ketones [15]. Actually, in the distillate formed after the removal of the solvent there was titrated with acid a volatile base the amount of which covered a considerable part of the unbalance of which we are speaking.

The elemental analysis of the phosphate of N-methyladrenaline prepared by us could not serve as the proof of structure of the substance since in its elemental composition this substance hardly differs from the phosphate of the original N-methyladrenalone. The latter salt was prepared specially from the base and phosphoric acid. Unfortunately, it turned out to be very similar in its properties to the metadrine phosphate and, although differing somewhat from the latter in the melting point (both salts melt unsharply with decomposition), failed to give a depression of melting point in a mixed sample. As might have been expected the substances being compared should differ greatly in the character of their light absorption in the ultraviolet region (the ketone should absorb in the region of longer waves), we determined and compared their absorption spectra which, as expected, turned out to be different, which fact proved the nonidentity of the two phosphates. As may be seen in the figure shown above, the phosphate of the hydrogenation product of N-methyladrenalone absorbs in the region of shorter waves, which fact indicates the absence of the carbonyl group in it.

EXPERIMENTAL

ω-Chloro-3,4-dihydroxyacetophenone (I) [5]. A mixture of a solution of 110 g (1 mole) of pyrocatechol in 150 ml of benzene with 124 g (1.1 mole) of chloroacetyl chloride and 9.5 g of phosphorus oxychloride was heated under a reflux condenser protected with a calcium chloride tube on a boiling water bath with mechanical stirring for 50 hrs(with interruptions). After cooling the reaction mixture to 5-10°, the resulting precipitate was filtered off, washed with benzene and was recrystallized from 150 ml of 2 N acetic acid with 1 g of carbon. The weight of the chloro ketone, dried at 110°, was 65-68 g. M. p. 172-173°.

From the benzene mother liquor after 10 days' standing in an open beaker* there separated an additional, considerable amount of the product from which, by recrystallization from 2 N acetic acid, there was obtained 40-42 g of the pure product with m. p. 171-173°. Total yield: 105-110 g (56-59%).

ω-Methylamino-3,4-dihydroxyacetophenone (II). A mixture of 52 g (0.28 mole) of the chloro ketone (I), 30 ml of ethanol and 40% aqueous solution of methylamine taken in the amount which corresponded to the content of 1.4 moles of the amine, was treated according to Stolz's directions [1], after which the reaction mixture was partly neutralized (with cooling) by means of 50 ml of concentrated hydrochloric acid and was left for 30 min in an ice bath under a layer of gasoline. Then, the precipitate was filtered off, washed with 0.1% solution of aqueous sodium hydrosulfite (until the filtrate ran colorless), followed by ethanol and ether. The yield of crude product was 36-38 g (71-73%). The purification was done by transformation of the substance into the hydrochloride and the recrystallization of the latter [2]. The yield of the hydrochloride was 65% of theoretical. The free base was precipitated from the solution of the hydrochloride with aqueous ammonia at pH 9-9.5.

ω-Amino-3,4-dihydroxyacetophenone (III). The reaction of dihydroxychloroacetophenone (I) and ammonia was run in a three-necked flask provided with a centrifugal stirrer with a packed gland closure, passing through a three-necked adapter set into the cork in the central neck of the flask. The side arm of the adapter was connected to a system for absorption of oxygen.** One of the side-necks of the flask carried a cork with a dropping funnel while the other one was provided with a glass tube which reached to the bottom of the flask and served for inlet of gaseous ammonia. All parts of the apparatus were connected sufficiently hermetically tightly. Into the flask was placed 60 ml of 25% aqueous ammonia and with external cooling by means of ice and salt there was introduced gaseous ammonia until complete saturation occurred. After that and with good stirring and in a weak stream of ammonia, there was added from the dropping funnel over 10-15 min a hot solution of 10 g of the chloro ketone (I) in 20 ml of methanol, while the cooling of the flask proceeded with the previous intensity. The mixing and the introduction of ammonia was continued for 6 hrs longer at room temperature, after which the reaction mixture was left overnight in an ammonia atmosphere. Then, the excess ammonia was removed by a strong current of nitrogen (finally with heating in a bath at temperature of 45-55°) and the flask contents were poured on a filter after a preliminary saturation with carbon dioxide. The precipitate was washed with ice water (until filtrate ran colorless), ethanol and ether. The crude product was purified through the hydrochloride, similarly to purification of adrenalone [2]. The yield of purified noradrenalone (free base) was 6.5-7.0 g (73-79%).

D,L-Adrenaline (IV) [8]. Hydrogenation of adrenalone was run in the apparatus commonly designed for this purpose using Raney nickel at room temperature. In order to create a slight positive pressure (0.2 atmos) in the system, the leveling bulb of the hydrogen reservoir was connected to the latter through a 2.5 m rubber tube and was suspended during the reaction some 2 m above the apparatus. The catalyst was prepared according to directions of [14] where it is called Raney nickel W-7. Into the hydrogenation vessel there was poured 50 ml of 2 N sodium hydroxide, the catalyst was added (this was prepared from 3.8 g of the alloy), the air was displaced from the system by means of hydrogen and, in a weak stream of hydrogen, there was charged 12.7 g of the adrenalone base. After 3-3.5 hrs the reaction was completed. The volume of the absorbed hydrogen exceeded by some 3-5% the calculated amount. The liquid, to which 0.1 g of sodium hydrosulfite was added immediately, was filtered off the catalyst through a glass filter into 45 ml of 4 N hydrochloric acid and the filtrate was made alkaline with ammonia solution under a layer of gasoline up to pH 9-9.5 (test with phenolphthalein paper). After 30-45 min standing in an ice bath, the precipitated adrenaline was filtered off, washed with water, ethanol and ether was dried in vacuo in the dark. Yield: 11.3-11.7 g (88-92%).

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* With rapid distillation of the solvent (even in vacuo) there is separated a product which is badly contaminated with tar.

** For this system we used two Drechsel flasks which were loosely filled with copper spirals moistened with saturated solution of ammonium chloride. The flasks were connected to each other by tubes which reached the bottom so that the system could work in either direction of flow.

For purification according to Savitskii [16], the adrenaline was dissolved in the minimum volume of aqueous sulfurous acid, the solution was filtered and made alkaline with ammonia under a layer of gasoline. The remaining operations in the isolation of the purified product did not differ from those described above. The yield was nearly colorless substance weighing about 11 g or 80-85% based on adrenalone.

D,L-α-Aminomethyl-3,4-dihydroxybenzyl alcohol (noradrenaline) (V). Noradrenalone (III) was hydrogenated analogously to adrenalone (see above). Absorption of hydrogen ceased after 3 hrs. After operations which were described above there was obtained noradrenaline in the form of a brownish microcrystalline powder in the yield of 76-80%.

ω-Dimethylamino-3,4-dihydroxyacetophenone (VI). A solution of 14 g of dihydroxychloroacetophenone (I) (0.075 mole) in 45 ml of hot methanol was added through a dropping funnel over 20-30 min to 0.18 mole of dimethylamine taken in the form of 30-35% solution, with stirring and cooling (temperature not above 5°). The mixture was left in a closed vessel for one day, after which it was evaporated in vacuo in a nitrogen stream to less than half the original volume for the removal of excess dimethylamine, and the residue was neutralized with ethanolic solution of hydrogen chloride (with Congo red). After 30 minutes' cooling to 0°, the precipitate was filtered off, treated in a beaker with a mixture of ethanol and acetone (1 : 2) twice, refiltered again and washed on the filter with acetone. The yield: 12.8-13.1 g (73-76%). Long prisms (from 16 parts of ethanol), with m. p. 210-212° with decomposition (after immersion of the capillary at 200°). (Literature data: m. p. 232° [11], 236° [12]). However, as shown by the analysis, the specimen prepared as described above and having m. p. 210-212°, is a pure hydrochloride of N-methyladrenalone.

Found %: Cl 15.39, 15.38. $C_{10}H_{13}O_3N \cdot HCl$. Calculated %: Cl 15.30.

After recrystallization from glacial acetic acid the substance separated in the form of prisms with m. p. 234-236° (with decomp.).

Mixed melting point of both salts was 234-236°, regardless of the composition of the mixture, which fact indicates the transition of the low melting modification into the high melting one during the heating of its mixtures with the latter.

For isolation of the base, 4.64 g of hydrochloride of N-methyladrenalone was mixed with 25 ml of dehydrated ethanol and to the mixture, heated nearly to boiling, there was added the carefully calculated amount of 1 M solution of sodium ethoxide in dehydrated ethanol. The hot solution was separated from sodium chloride by filtration and the filtrate was evaporated to dryness in vacuo in a stream of nitrogen with feeble heating. The residue was treated 4 times with 15 ml of anhydrous isopropyl alcohol at 60-65° (tar formation occurs at higher temperatures) and the resulting extract was cooled. The resulting oil transformed itself rapidly into an amorphous powder which was filtered off, washed on the filter with a small volume of cooled isopropyl alcohol and was immediately transferred into a vacuum desiccator (the product liquefies in air if it contains any solvent). The yield of dry base was 2.8-2.9 g (72-74%). From the mother liquor there was regenerated the hydrochloride with m. p. 208-210°, by neutralization with an alcoholic solution of hydrogen chloride.

The base of N-methyladrenalone is a yellowish cream powder, which is rather readily soluble in methanol, ethanol and water, especially when heated. From a hot solution in isopropyl alcohol it separates on cooling but at times in the form of a rapidly solidifying oil. It melts unsharply with decomposition at temperatures above 130°. The purified specimen with a sharp melting point was unobtainable and for this reason the elemental analysis of this substance was not run. The equivalent of the substance was determined by potentiometric titration with acid.

Found: equivalent in respect to acid 197.5. $C_8H_7O_3N(CH_3)_2$. Calculated: equivalent in respect to acid 195.2.

By neutralization of the base with hydrogen chloride or oxalic acid in an alcoholic solution there are isolated, respectively, the hydrochloride with m. p. 210-212° (decomp.) or the oxalate with m. p. 236-237°. The latter is the neutral salt, not the acid salt as indicated in the literature [13], which fact was established by analysis, by precipitation of calcium oxalate and its titration with permanganate solution.

Found %: $H_2C_2O_4$ 19.21, 18.64. $C_{10}H_{13}O_3N \cdot {}^1/_2 H_2C_2O_4$. Calculated %: $H_2C_2O_4$ 18.80.

The phosphate of N-methyladrenalone was prepared by mixing the solutions of the base and the calculated amounts of crystalline phosphoric acid in ethanol. After recrystallization from glacial acetic acid, it formed a colorless finely crystalline powder with m. p. 203-205° (decomp.).

Found %: P 10.80, 10.63. $C_{10}H_{13}O_3N \cdot H_3PO_4$. Calculated %: P 10.58.

ω-Dimethylamino-3,4-diacetoxyacetophenone (VIII). To a mixture of 8 ml of anhydrous acetic acid and 5 ml of acetyl chloride, heated to 60-70°, there was added dropwise a solution of 1.95 g of the base of N-methyladrenalone in 8 ml of anhydrous acetic acid. After termination of the vigorous evolution of hydrogen chloride, the solution was left overnight in a closed vessel. Then the solvent was distilled as completely as possible in vacuo with mild heating. Traces of acetic acid were removed by 2-3 dissolutions of the resulting glue-like product in 15 ml of anhydrous butanol and its distillation in vacuo. After heating on a boiling water bath in good vacuum (1-2 mm), the residue solidified. It was dissolved in 5 ml of isopropyl alcohol. From this solution, after dilution with 10 ml of dry ethyl acetate, addition of a seed crystal, addition of 1-2 ml of anhydrous ether and strong cooling, there separated a crystalline precipitate, which was again recrystallized from a mixture of isopropyl alcohol and ethyl acetate. Yield: 1.4-1.5 g (44-48%). Short needles with m. p. 170-172°. The same product was obtained from the hydrochloride of N-methyladrenalone with acetyl chloride in glacial acetic acid, in the yield of 60%.

From the mother liquors after the separation and crystallization of the above hydrochloride, there was isolated an additional amount of the substance in the form of the base by evaporation of the solvent in vacuo, solution of the precipitate in a small volume of water, addition of soda solution until alkaline and rapid extraction with benzene.

Found %: Cl 11.32, 11.30. $C_{14}H_{17}O_5N \cdot HCl$. Calculated %: Cl 11.23.

The extract, dried with anhydrous sodium sulfate, was concentrated in vacuo until the beginning of crystallization and was then diluted with 4-5 volumes of petroleum ether. The yield of crystals was 0.5-0.6 g (18-21%). The total yield of the diacetyl derivative during its preparation from the hydrochloride of N-methyladrenalone was 78-84% of theoretical. The base formed colorless needles with m. p. 97-98° (from benzene with petroleum ether). It yellows rapidly in air, being transformed into the base of N-methyladrenalone.

Found %: C 60.80, 60.92; H 6.23, 6.24; N 4.98, 5.18. $C_{14}H_{17}O_5N$. Calculated %: C 60.22; H 6.13; N 5.01.

The picrate (from equimolar amounts of the base and trinitrophenol in benzene) formed bright yellow elongated hexagonal plates (from methanol) with m. p. 141.5-143°. It is readily soluble in acetone, glacial acetic acid and hot ethanol, insoluble in benzene and ether.

Found %: N 11.13, 11.04. $C_{20}H_{20}O_{12}N_4$. Calculated %: N 11.03.

N-Methyladrenaline (VII). a) Hydrogenation of N-methyladrenalone (VI) with palladium catalyst. A solution of 2 g (0.01 mole) of N-methyladrenalone base in 30 ml of methanol was shaken with 0.6 g of palladium deposited on carbon (5% Pd) [17] in hydrogen atmosphere with residual excess pressure of 0.2 atmos (see preparation of adrenaline) at room temperature. The absorption of hydrogen stopped after 48 hrs. The solution was filtered from the catalyst and was evaporated in vacuo in a stream of nitrogen to dryness in order to remove the volatile bases, the exiting vapors and gases being led through a Tishchenko flask containing 0.2 N standardized sulfuric acid solution. The dry residue was dissolved in 20 ml of anhydrous ethanol and the solution was added to 1 g of crystalline phosphoric acid dissolved in 5 ml of anhydrous ethanol. The mixture, if alkaline, was acidified to litmus with an alcoholic solution of phosphoric acid and the separated phosphate was filtered off and washed with a mixture of ethanol and acetone. Yield: 2.4 g (80%). M. p. 181-183° (with decomposition) (from glacial acetic acid with methanol and ether).

Found %: N 4.76, 4.63; P 10.65, 10.70. $C_{10}H_{15}O_3N \cdot H_3PO_4$. Calculated %: N 4.75; P 10.50.

The contents of the Tishchenko absorption flask were carefully titrated with 0.1 N sodium hydroxide with Methyl orange indicator. The content of volatile bases, calculated from the results of titration and being evidently dimethylamine, comprised 0.9 mole in one experiment, i. e., 9% of the amino ketone used in the reaction.

b) Hydrogenation of N-methyladrenalone(VI) with Raney nickel. A solution of 3.9 g (0.02 mole) of methyladrenalone base in 50 ml of methanol was shaken with Raney nickel, prepared from 1 g of the alloy [14], in hydrogen atmosphere at room temperature and 0.2 atmos of excess pressure. Over 3 hrs less than 5% of calculated volume of hydrogen was taken up. After 15 ml of 2 N solution of sodium hydroxide had been added to the solution (0.03 mole NaOH), the absorption of hydrogen proceeded rapidly and was completed in 2.5 hrs with the absorbed volume exceeding the calculated volume by 12%. After separation from the catalyst and distillation of major part of the solvent, the resulting solution residue was neutralized to litmus with an alcoholic solution of phosphoric acid and was evaporated to dryness in vacuo. The residue was treated with hot glacial acetic acid, the solution was filtered while hot from sodium phosphate and, after dilution with anhydrous ethanol and ether, and cooling, there precipitated from it a 4.02 g yield of N-methyladrenaline (68.5%).

SUMMARY

1. The directions for preparation of adrenaline, noradrenaline and N-methyladrenaline were improved and refined.

2. The previously unknown base of N-methyladrenalone was isolated and its phosphate was prepared for the first time. The properties and the composition of the hydrochloride and the oxalate were ascertained.

3. Diacetyl derivative of N-methyladrenalone was prepared for the first time and analyzed in the form of the free base, hydrochloride and picrate.

4. Phosphate of D,L-N-methyladrenaline was prepared for the first time, this being the sole presently known crystalline preparation of this compound.

5. The catalytic influence of hydroxyl ions on the rate of hydrogenation of adrenalone and its analogs was shown. A supposition was made as to the mechanism of this effect.

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* In Russian.

** Original Russian pagination. See C. B. translation.

SYNTHESIS OF THIACARBOCYANINES WITH UNSATURATED RADICALS AS SUBSTITUENTS

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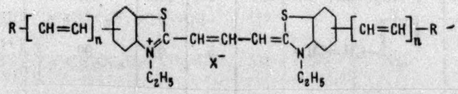
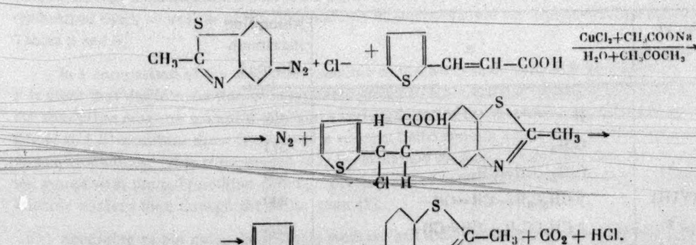
Thiacyanine dyes containing unsaturated groupings in the benzothiazole nucleus with the general formula



where n = 1 or 2 ; R= CH_3, C_6H_5, V - C_6H_4 or

have not been described to this time. One may expect that, owing to the conjugation of unsaturated groupings with the polymethine chromophore of the thiacarbocyanine through the atom of nitrogen or sulfur [1, 2] of the thiazole ring, the conjugation chain would be lengthened as the result of which there should occur a deepening of the color of the dye. With this purpose in mind we synthesized according to the Meerwein reaction [3-11] the necessary bases by interaction of benzothiazolyldiazonium chlorides with unsaturated compounds. Heterocyclic diazo compounds had not been used in the Meerwein reaction previously. Several thiacarbocyanines containing unsaturated groupings in 6,6'-positions had been prepared by us previously [12].

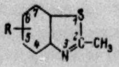
In the present work we describe the synthesis of 2-methylbenzothiazoles containing various unsaturated groups in 5- or 6-positions. In the reaction of diazotized 2-methyl-5-aminobenzothiazole and 2-methyl-6-aminobenzothiazole with coumarin, cinnamic, p-methoxycinnamic, p-methylcinnamic and α-thienylacrylic acids there were prepared seven new bases (Table 1) containing unsaturated substituents in the benzothiazole ring. Synthesis of the bases may be shown by the following scheme:



Evolution of nitrogen and carbon dioxide was observed during the synthesis. From the reaction mixture there were isolated 2-methylchlorobenzothiazoles, 2-methylbenzothiazole and chloroacetone, besides the benzothiazoles with unsaturated groups. The bases were purified by chromatography on aluminum oxide with a subsequent

TABLE 1

Substituted 2-Methylbenzothiazoles



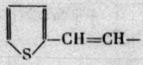
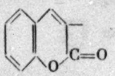
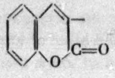
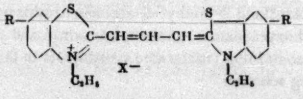
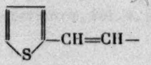
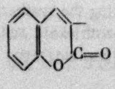
No. of substance	R	Substituent position	Yield (in %)	Melting point
(I)	$C_6H_5-CH=CH-$	5	20	138–139°
(II)	$p\text{-}CH_3C_6H_4-CH=CH-$	5	11.7	128–129
(III)	$p\text{-}CH_3C_6H_4-CH=CH-$	6	16.8	155–156
(IV)	$p\text{-}CH_3OC_6H_4-CH=CH-$	5	14.6	151
(V)		5	9.3	90
(VI)		5	8.3	218–219
(VII)		6	5.4	178–179

TABLE 2

Dyes



No. of substance	R	Absorption maximum (in $m\mu$)
—	H	558
—	C_6H_5-	574
*	$C_6H_5-CH=CH-$	595
(VIII)	$p\text{-}CH_3C_6H_4-CH=CH-$	600
*	$p\text{-}CH_3OC_6H_4-CH=CH-$	605
*		606
(IX)		582

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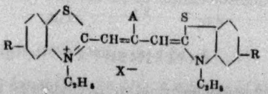
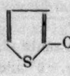
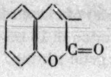
* Dyes which were prepared previously [12].

TABLE 3

Dyes



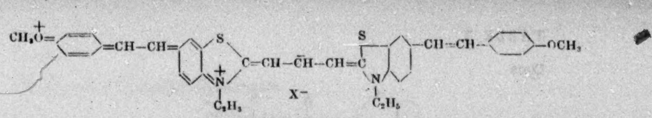
No. of substance	R	Absorption maximum (mμ)		
		A		
		H	CH_3	C_2H_5
—	H	558	543	547
—	C_6H_5—	567	553	558
(X) (XI) (XII)	C_6H_5—CH=CH—	578	565	567
(XIII)	p-$CH_3C_6H_4$—CH=CH—	582	—	—
(XIV) (XV) (XVI)	p-$CH_3OC_6H_4$—CH=CH—	582	568	574
(XVII) (XVIII) (XIX)	 —CH=CH—	584	567	572
(XX) (XXI)		570	556	—

crystallization from alcohol or ligroine. The low yield of the bases is caused by a number of side reactions: formation of 2-methylchlorobenzothiazoles, azo compounds as well as tarry products whose composition and structure were not determined by us.

By the action of alkylating agents the resulting bases were transformed into quaternary salts. The latter were introduced into a condensation with ortho esters of carboxylic acids in pyridine. The absorption maxima of the synthesized dyes, as well as of the unsubstituted thiacarbocyanine and diphenylthiacarbocyanines are shown in Tables 2 and 3.

In a comparison of the absorption maxima of the synthesized dyes with the unsubstituted thiacarbocyanine it is clear that the introduction of unsaturated groups in 5,5'- and 6,6'-positions of thiacarbocyanine strongly shifts the absorption maxima toward the longer wavelength end of the spectrum. For thiacarbocyanines with unsaturated groups in 6,6'-positions there is observed a stronger bathochromic effect than for the corresponding 5,5'-substituted thiacarbocyanines. This phenomenon may be explained evidently by the fact that the conjugation of the unsaturated groups with the polymethine chromophore is realized considerably better through a nitrogen atom of the benzothiazole nucleus than through the sulfur atom [1].

According to our data, the methyl, methoxy and methylmercapto groups introduced into the para-position of the phenyl radical in 6,6'-diphenylthiacarbocyanine do not cause a deepening of the color. However, it is clear from Tables 2 and 3 that introduction of methyl or methoxy group into the para-position of the styryl radical causes a certain shift of the absorption maximum toward the longer wavelength end of the spectrum. This shows that the presence of vinylene groups in 5,5'- or 6,6'-positions of thiacarbocyanine aids the electron displacement, which, for example, in 3,3'-diethyl-6,6'-di-(p-methoxystyryl)-thiacarbocyanine (Table 2) may be represented thus:



EXPERIMENTAL

General technique of synthesis of 2-methylbenzothiazoles containing unsaturated groupings. Into a flask with a mechanical stirrer, thermometer and an outlet tube connected to a Tishchenko absorption flask containing a solution of barium hydroxide, there was placed 0.1 mole of unsaturated acid, 120-180 ml of acetone, 0.2 mole of crystalline sodium acetate and 0.03 mole of cupric chloride ($CuCl_2 \cdot 2H_2O$). The mixture was cooled with stirring to −2° to −5° and to it was added in small portions over 15-30 min a solution of benzothiazolyldiazonium chloride, prepared by solution of 0.1 mole of the amine in 25 ml of concentrated hydrochloric acid and 20 ml of water with subsequent diazotization with 0.11 mole of sodium nitrite in 12 ml of water. After that the mixture was stirred for 1-1.5 hr at −2°, after which its temperature was raised gradually until carbon dioxide began to evolve. The reaction mixture was stirred for 2-3 hrs at room temperature and was subjected to steam distillation on the following day. Acetone, chloroacetone and 2-methylchlorobenzothiazole distilled. The dark oil remaining in the distilling flask and solidifying on cooling was dissolved in chloroform and subjected to chromatography on aluminum oxide. The base was eluted with chloroform or benzene. The almost colorless zone formed by the base fluoresced with light yellow color in ultraviolet light. This zone was collected separately, the solvent was distilled off and the residue of the solvent was evaporated on a water bath. Usually a viscous yellow oil was obtained which crystallized instantly. Finally, the base was crystallized from alcohol or ligroine with use of animal charcoal.

2-Methyl-5-styrylbenzothiazole (I). 2-Methyl-5-aminobenzothiazole (16.4 g, 0.1 mole) was dissolved in 25 ml of concentrated hydrochloric acid and 20 ml of water, cooled to −5° and diazotized with 7.5 g (0.11 mole) of sodium nitrite in 12 ml of water. A mixture of 14.8 g (0.1 mole) of cinnamic acid, 120 ml of acetone, 27.2 g (0.2 mole) of sodium acetate and 5.1 g (0.03 mole) of cupric chloride in 10 ml of water was cooled to −2° and to this mixture there was added the diazonium chloride with energetic stirring. At 9° a slow evolution of gaseous products began and continued for one hour.

A viscous yellow oil was obtained after chromatography; it crystallized instantly. The base was recrystallized from 140 ml of methanol with the aid of animal charcoal. Yield: 2.5 g. Crystals with light yellow color; m. p. 138-139°; readily soluble in benzene, chloroform, acetone, ether, and difficultly soluble in alcohol.

Found %: S 12.52, 12.74. $C_{16}H_{13}NS$. Calculated %: S 12.71.

2-Methyl-5-(p-methylstyryl)-benzothiazole (II). Into a flask was placed 3.7 g (0.023 mole) of p-methylcinnamic acid, 60 ml of acetone, 6.2 g (0.075 mole) of sodium acetate and 1.32 g (0.0077 mole) of cupric chloride in 5 ml of water. To the cooled mixture (−2°) there was added with energetic stirring the diazonium chloride prepared from 3.65 g of 2-methyl-5-aminobenzothiazole, 5.7 ml of hydrochloric acid, 5 ml of water and 1.68 g of sodium nitrite in 3 ml of water. The evolution of gaseous products began at 16° and continued for 1 hr. The mixture was stirred for 1 hr at room temperature. The base was recrystallized from 80 ml of methanol. Yield: 0.68 g. Colorless crystals with m. p. 128-129°.

Found %: S 12.18, 11.92. $C_{17}H_{15}NS$. Calculated %: S 12.07.

2-Methyl-6-(p-methylstyryl)-benzothiazole (III). A mixture of 3.5 g (0.02 mole) of p-methylcinnamic acid, 60 ml of acetone, 5.8 g (0.04 mole) of sodium acetate and 1.1 g (0.0066 mole) of cupric chloride in 4 ml of water was cooled to −2°. To the cooled mixture there was added the diazonium salt solution prepared by diazotization of 3.46 g of 2-methyl-6-aminobenzothiazole in 5.4 ml of hydrochloric acid and 4 ml of water with 1.6 g of sodium nitrite in 3 ml of water. Evolution of carbon dioxide began at 20° and lasted for 1.5 hr. The yield, after recrystallization from methanol, 0.93 g. Colorless crystals with m. p. 155-156°.

Found %: S 11.98, 11.83. $C_{17}H_{15}NS$. Calculated %: S 12.07.

2-Methyl-5-(p-methoxystyryl)-benzothiazole (IV). 2-Methyl-5-aminobenzothiazole (16.4 g) was diazotized as indicated above. Into a flask there was placed 17.8 g (0.1 mole) of p-methoxycinnamic acid, 180 ml of acetone, 27.2 g (0.2 mole) of sodium acetate and 5.1 g of cupric chloride in 20 ml of water. After the addition of the diazonium chloride an intense evolution of gaseous products began (at 0°) and lasted for 2 hrs. The base was crystallized from 130 ml of alcohol with the use of animal charcoal. Yield: 4.1 g. Light yellow crystals with m. p. 151°.

Found %: S 11.55, 11.77. $C_{17}H_{15}ONS$. Calculated %: S 11.39.

2-Methyl-5-(α-thienylvinyl)-benzothiazole (V). A mixture of 15.4 g (0.1 mole) of α-thienylacrylic acid, 180 ml of acetone, 27.2 g (0.2 mole) of sodium acetate and 5.1 g (0.03 mole) of cupric chloride in 20 ml of water was cooled to −2° and to the cooled mixture there was added benzothiazolyldiazonium chloride, prepared by diazotization of 16.4 g (0.1 mole) of 2-methyl-5-aminobenzothiazole. Evolution of gaseous products began at 0° and continued for 2.5 hrs. The base was crystallized from ligroine(b. p. 60-90°) for purification. Yield: 2.3 g. Colorless crystals with m. p. 90°.

Found %: S 24.93, 25.16. $C_{14}H_{11}NS_2$. Calculated %: S 24.90.

2-Methyl-5-coumarinylbenzothiazole (VI). Into a flask there was placed 7.3 g (0.05 mole) of coumarin, 50 ml of acetone, 13.6 g (0.1 mole) of cupric chloride in 5 ml of water and the mixture was cooled to −2°, after which there was added to it the diazonium chloride, prepared by diazotization of 8.2 g of 2-methyl-5-aminobenzothiazole. Evolution of nitrogen began at 15° and continued for 1.5 hr. The base was recrystallized from alcohol. Yield: 1.2 g. Colorless needles with m. p. 203-204°.

Found %: S 10.84, 11.12. $C_{17}H_{11}O_2NS$. Calculated %: S 10.92.

2-Methyl-6-coumarinylbenzothiazole (VIII) was prepared analogously to 2-methyl-5-coumarinylbenzothiazole. Evolution of nitrogen began at 12° and continued for 1 hr and 15 min. Yield: 0.75 g. Colorless crystals with m. p. 178-179°.

Found %: S 10.73, 10.92. $C_{17}H_{11}O_2NS$. Calculated %: S 10.92.

Quaternary Salts

The quaternary salts were prepared by the usual method of heating the bases with ethyl ester of p-toluenesulfonic acid or with diethyl sulfate.

Ethyl p-toluenesulfonate of 2-methyl-5-styrylbenzothiazole. A mixture of 0.75 g (0.003 mole) of 2-methyl-5-styrylbenzothiazole and 1.2 g (0.006 mole) of ethyl ester of p-toluenesulfonic acid was heated in a flask with an air condenser on a paraffin bath at 160° (in the bath). The flask contents were dissolved in 150 ml of boiling water, the solution was extracted with benzene, boiled with animal charcoal and evaporated on a water bath. For complete removal of water, the residue was heated to 130° with stirring. Yield: 1.25 g (92.5%).

Ethiodide of 2-methyl-5-(p-methoxystyryl)-benzothiazole. 2-Methyl-5-(p-methoxystyryl)-benzothiazole (0.56 g; 0.002 mole) and 0.32 g of diethyl sulfate (0.0021 mole) were heated for 4.5 hrs at 135-140° (in the paraffin bath). 20 ml of boiling water was added to the contents of the flask. The undissolved residue (0.15 g) which turned out to be 2-methyl-5-(p-methoxystyryl)-benzothiazole, was filtered off and washed with water. The aqueous solution was concentrated to 10 ml and to it was added 1.5 g of dry potassium iodide with stirring. The light yellow crystals which precipitated were filtered off, washed with 5 ml of cold water and dried. Yield: 0.45 g (51%). Then, the ethiodide was recrystallized from alcohol. Colorless crystals with m. p. 254-255°.

Found %: I 28.30, 28.11. $C_{19}H_{20}ONSI$. Calculated %: I 29.06.

Dyes

3,3'-Diethyl-6,6'-bis-(p-methylstyryl)-thiacarbocyanine perchlorate (VIII). A mixture of 0.052 g (0.0002 mole) of 2-methyl-6-(p-methylstyryl)-benzothiazole and 0.08 g (0.0004 mole) of ethyl ester of p-toluenesulfonic acid was heated on an oil bath for 6 hrs at 145-155°. The quaternary salt was dissolved in 1 ml of pyridine, treated with 0.3 g of ethyl orthoformate and refluxed for 20 min. The dye was precipitated with hot aqueous solution of sodium perchlorate and was recrystallized from alcohol. Small bronze-colored crystals; m. p. 229° (with decomp.). Yield: 0.04 g (30%).

Found %: N 4.06, 4.04. $C_{39}H_{37}O_4N_2S_2Cl$. Calculated %: N 4.17.

3,3'-Diethyl-6,6'-dicoumarinylthiacarbocyanine p-toluenesulfonate (IX) was prepared by refluxing for 15 min a mixture of 0.44 g (0.001 mole) of ethyl p-toluenesulfonate of 2-methyl-6-coumarinylbenzothiazole and 0.5 g of ethyl orthoformate in 3 ml of pyridine. The dye was precipitated with ether and was recrystallized from alcohol. Yield: 0.12 g (28%). Violet crystals with m. p. 230-232°.

Found %: S 11.94, 11.53. $C_{46}H_{36}O_7N_2S_3$. Calculated %: S 11.63.

3,3'-Diethyl-5,5'-distyrylthiacarbocyanine p-toluenesulfonate (X). A mixture of 0.45 g (0.001 mole) of ethyl p-toluenesulfonate of 2-methyl-5-styrylbenzothiazole, 0.5 g (0.003 mole) of ethyl orthoformate and 3 ml of pyridine was refluxed for 50 min. The dye was precipitated with ether and was recrystallized from alcohol. Yield: 0.13 g (34.6%). Violet crystals with m. p. 257-260°.

Found %: S 13.32, 13.09. $C_{44}H_{40}O_3N_2S_3$. Calculated %: S 13.54.

3,3'-Diethyl-5,5'-distyryl-9-methylthiacarbocyanine iodide (XI). 2-Methyl-5-styrylbenzothiazole (0.25 g, 0.001 mole) and 0.16 g of diethyl sulfate (0.0105 mole) were heated for 2 hrs at 125-130°. To the resulting quaternary salt there was added 0.32 g of ethyl orthoacetate, 2 ml of pyridine and 0.05 g of acetic anhydride and the mixture was refluxed for 15 min. The dye was precipitated with ether, dissolved in alcohol, treated with an aqueous solution of potassium iodide and recrystallized from alcohol. Yield: 0.06 g (16.8%). Violet crystals with m. p. 273-274°.

Found %: I 17.75, 17.80. $C_{38}H_{35}N_2S_2I$. Calculated %: I 17.86.

3,3',9-Triethyl-5,5'-distyrylthiacarbocyanine iodide (XII) was prepared analogously by heating 0.25 g (0.001 mole) of 2-methyl-5-styrylbenzothiazole and 0.16 g of diethyl sulfate for 3 hrs at 130-140°. To the quaternary salt there was added 0.26 g of ethyl orthopropionate, 2 ml of pyridine and 0.05 g of acetic anhydride and the mixture was refluxed for 15 min. Yield: 0.08 g (22%). Violet crystals with m. p. 264-265°.

Found %: I 17.32, 17.29. $C_{39}H_{37}N_2S_2I$. Calculated %: I 17.52.

3,3'-Diethyl-5,5'-bis-(p-methylstyryl)-thiacarbocyanine ethyl sulfate (XIII). A mixture of 0.26 g (0.001 mole) of 2-methyl-5-(p-methylstyryl)-benzothiazole and 0.16 g of diethyl sulfate was heated for 3 hrs at 130-135°. To the resulting solid mass there was added 3 ml of pyridine, 0.5 g of ethyl orthoformate and the mixture was refluxed for 20 min. The resulting crystalline precipitate was filtered off and recrystallized from alcohol. Green needles with metallic sheen; m. p. 292-293°. Yield: 0.21 g (58%).

Found %: S 12.94, 12.84. $C_{41}H_{42}O_4N_2S_3$. Calculated %: S 13.28.

3,3'-Diethyl-5,5'-bis-(p-methoxystyryl)-thiacarbocyanine bromide (XIV) was prepared analogously by heating 0.28 g (0.001 mole) of 2-methyl-5-(p-methoxystyryl)-benzothiazole and 0.16 g of diethyl sulfate 3 hrs at 130-135°. To the resulting quaternary salt there was added 0.5 g of ethyl orthoformate, and 3 ml of pyridine and the mixture was refluxed for 40 min. The dye was precipitated with ether and was dissolved in 160 ml of alcohol. The resulting precipitate was filtered off, washed with alcohol and with ether. Yield: 0.21 g (54%); m. p. 280-281°.

A solution of 0.1 g of the dye in 1:1 alcohol-pyridine mixture was heated to boiling and was precipitated with a hot aqueous solution of potassium bromide. After recrystallization from alcohol, the yield was 0.06 g. Dark green plates with m. p. 235-236°.

Found %: Br 11.34, 11.50. $C_{39}H_{37}O_2N_2S_2Br$. Calculated %: Br 11.28.

3,3'-Diethyl-5,5'-bis-(p-methoxystyryl)-9-methylthiacarbocyanine iodide (XV). A mixture of 0.28 g of 2-methyl-5-(p-methoxystyryl)-benzothiazole and 0.16 g of diethyl sulfate was heated for 3 hrs at 130-135°. To the solid brown mass there was added 0.32 g of ethyl orthoacetate, 2 ml of pyridine and 0.05 g of acetic anhydride and the mixture was refluxed for 40 min. Yield: 0.12 g (30%); m. p. 189-190°. Then the dye was dissolved in a mixture of pyridine and alcohol and was precipitated with potassium iodide. Yield: 0.05 g; m. p. 244-245°. Small crystals with a bronze sheen.

Found %: I 16.64, 16.41. $C_{40}H_{39}O_2N_2S_2I$. Calculated %: I 16.49.

3,3',9-Triethyl-5,5'-bis-(p-methoxystyryl)-thiacarbocyanine ethyl sulfate (XVI) was prepared analogously by heating 0.28 g of 2-methyl-5-(p-methoxystyryl)-benzothiazole and 0.16 g of diethyl sulfate for 3.5 hrs at 130-135°. To the resulting solid mass there was added 2 ml of pyridine, 0.26 g of ethyl orthopropionate and 0.05 g of acetic anhydride and the mixture was refluxed for 40 min. The dye was precipitated with ether and was recrystallized from alcohol. Yield: 0.07 g (17.2%). Violet crystals with m. p. 252-255°.

Found %: S 12.14, 11.85. $C_{43}H_{46}O_6N_2S_3$. Calculated %: S 12.26.

3,3'-Diethyl-5,5'-bis-(α-thienylvinyl)-thiacarbocyanine p-toluenesulfonate (XVII). Ethyl p-toluenesulfonate (0.46 g) of 2-methyl-5-(α-thienylvinyl)-benzothiazole, 0.5 g of ethyl orthoformate and 3 ml of pyridine were refluxed for 40 min. The dye was precipitated with ether and was recrystallized from alcohol. Yield: 0.18 g; m. p. 220° (with decomp.). Small crystals of dark green color.

Found %: S 20.94, 20.97. $C_{40}H_{36}O_3N_2S_5$. Calculated %: S 21.25.

3,3'-Diethyl-5,5'-bis-(α-thienylvinyl)-9-methylthiacarbocyanine iodide (XVIII). A mixture of 0.26 g of 2-methyl-5-(α-thienylvinyl)-benzothiazole and 0.16 g of diethyl sulfate was heated for 3 hrs at 130-135°. To the solid mass there was added 2 ml of pyridine, 0.32 g of ethyl orthoacetate and 0.05 g of acetic anhydride and the mixture was refluxed for 40 min. The resulting precipitate of the dye was filtered off and washed with alcohol and ether. Yield: 0.15 g (29%). Violet crystals with m. p. 292-293°. The ethyl sulfate was converted into the iodide and this was recrystallized from alcohol. Yield: 0.08 g. Crystals with dark green color; m. p. 227-228°.

Found %: I 17.54, 17.64. $C_{34}H_{31}N_2S_4I$. Calculated %: I 17.59.

3,3',9-Triethyl-5,5'-bis-(α-thienylvinyl)-thiacarbocyanine iodide (XIX) was prepared by heating a mixture of 0.26 g of the base and 0.16 g of diethyl sulfate for 3.5 hrs at 130-135°. To the quaternary salt there was added 0.26 g of ethyl orthopropionate, 2 ml of pyridine and 0.05 g of acetic anhydride and the mixture was refluxed for 50 min. The dye was precipitated with ether, dissolved in 100 ml of alcohol, treated with aqueous solution of potassium iodide and recrystallized from alcohol. Yield: 0.09 g. Crystals with bronze colors; m.p. 208-209°.

Found %: I 16.95, 16.92. $C_{35}H_{33}N_2S_4I$. Calculated %: I 17.25.

3,3'-Diethyl-5,5'-dicoumarinylthiacarbocyanine p-toluenesulfonate (XX). A mixture of 0.49 g of ethyl p-toluenesulfonate of 2-methyl-5-coumarinylbenzothiazole, 0.5 g of ethyl orthoformate and 3 ml of pyridine was refluxed for 30 min. The resulting precipitate of the dye was filtered off and recrystallized from alcohol. Yield: 0.13 g (31%). Violet crystals with m. p. 255-257°.

Found %: S 10.87, 10.78. $C_{46}H_{36}O_7N_2S_3$. Calculated %: S 11.63.

3,3'-Diethyl-5,5'-dicoumarinyl-9-methylthiacarbocyanine ethyl sulfate (XXI) was prepared by heating a mixture of 0.29 g of 2-methyl-5-coumarinylbenzothiazole and 0.16 g of diethyl sulfate for 1 hr at 160-170°. To the solid mass there was added 0.32 g of ethyl orthoacetate, 2 ml of pyridine and 0.05 g of acetic anhydride and the mixture was refluxed for 20 min. The dye was precipitated with ether and was recrystallized from alcohol. Yield: 0.06 g. Green crystals with metallic sheen; m. p. 272-273°.

Found %: S 11.84, 11.92. $C_{42}H_{36}O_8N_2S_3$. Calculated %: S 12.10.

SUMMARY

1. Seven new derivatives of benzothiazole, containing unsaturated groups in 5- or 6- positions, were prepared by the reaction of arylacrylic acids or coumarin with the diazotized 2-methyl-5-amino- or 2-methyl-6-aminobenzothiazoles.

2. Several quaternary salts were prepared by heating the bases with alkylating agents.

3. Fourteen thiacarbocyanines, containing unsaturated groups in 5- or 6-positions, were prepared by condensation of the quaternary salts with ortho esters of carboxylic acids in pyridine.

4. It was shown that the introduction of unsaturated groups into 5,5'- or 6,6'-positions of the thiacarbocyanine molecule produces a strong bathochromic effect.

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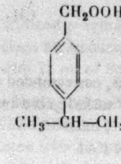
* Original Russian pagination. See C. B. translation.

LIQUID PHASE OXIDATION OF ALKYLAROMATIC HYDROCARBONS WITH ATMOSPHERIC OXYGEN

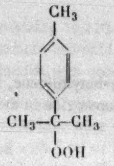
OXIDATION OF p-CYMENE AND p-SEC-BUTYLTOLUENE

V. V. Fedorova and P. G. Sergeev

According to some data [1, 2] the action of oxygen in autoxidation of p-cymene is directed to the primary α-carbon. A hydroperoxide of p-cymene was isolated which corresponded to formula (I) [2] but no characterization of this hydroperoxide was given.



(I)



(II)

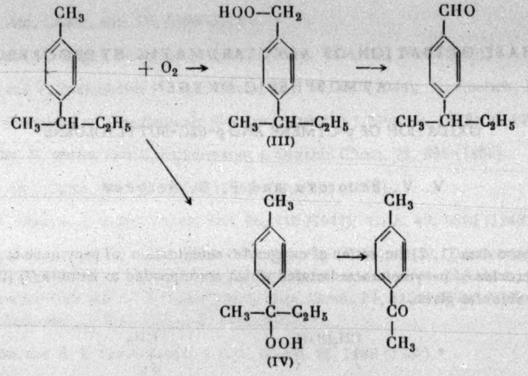
On the other hand, it was found [3] that in the oxidation of p-cymene in emulsion with aqueous alkali the sole primary oxidation product is a hydroperoxide which contains active oxygen at the tertiary α-carbon atom (II). The hydroperoxide of such structure was also obtained later [4] in the homogeneous liquid phase oxidation of p-cymene with a catalyst at 95°. However, according to other authors [5, 6], oxidation of p-cymene proceeds at both the primary and the tertiary α-carbon atoms.

In 1953 we set up some experiments for the study of oxidation of p-cymene by atmospheric oxygen in the presence of a small amount of a catalyst which was soluble in the hydrocarbon, as well as in an aqueous alkaline emulsion, in order to isolate the resulting hydroperoxides and to establish their structures. In both cases there was isolated from the oxidized hydrocarbon only the tertiary hydroperoxide (II), whose structure was established by the reaction with sulfuric acid. Along with the hydroperoxide there were found among the oxidation products in oxidized p-cymene some cumyl aldehyde and p-methylacetophenone, while after oxidation in the homogeneous medium there was also isolated some cumic acid. In the emulsion oxidation, the aqueous layer, which contained both the emulsifier and the acidic products of reaction, was not examined by us.

The results obtained by us give basis for considering that in the oxidation of p-cymene the oxygen reacts at both the primary and the tertiary α-carbon atoms of the side chains, forming hydroperoxides of two types. The direction of the reaction is not changed by change in the method of oxidation. At the end of our investigation there was published a paper [7] in which it was found that the relative activity of the methyl and the isopropyl groups in the p-cymene relative to oxygen and in emulsion and in photochemical oxidation at 85° stands in the ratio of 1 : 3.5.

p-sec-Butyltoluene, analogous to p-cymene, has one primary and one tertiary α-carbon atom, which are capable of being oxidized. No literature data exist concerning the oxidation of this hydrocarbon.

We ran the oxidation of p-sec-butyltoluene in homogeneous medium under the same conditions as in the oxidation of p-cymene. In the reaction mixture after the oxidation there were found, in addition to the hydroperoxide, some p-sec-butylbenzaldehyde and p-methylacetophenone, which fact speaks for oxidation of p-sec-butyltoluene yielding the hydroperoxides of both types (III) and (IV). The reaction scheme may be represented as:



The hydroperoxide of p-sec-butyltoluene, isolated by us, corresponded to formula (IV), which was confirmed by the decomposition of this hydroperoxide in the presence of sulfuric acid into p-cresol and methyl ethyl ketone.

EXPERIMENTAL

Oxidation of p-cymene. Prior to oxidation p-cymene was washed with sulfuric acid (d 1.84), water, sodium hydroxide solution and water, and after drying was carefully fractionated.

B. p. 30-30.5° at 2 mm, $n^{20}D$ 1.4906, d_4^{20} 0.8579. According to data of [8]: b. p. 177.25° at 760 mm, $n^{20}D$ 1.4909, d_4^{20} 0.8573.

The oxidation was run in a cylindrical flask with a widened upper portion, provided with a reflux condenser (connected to a trap), a thermometer, stirrer and a capillary tube for air inlet.

In the homogeneous oxidation experiments, p-cymene was charged into the flask along with manganese resinate (5 mg per mole) and a few drops of 97% isopropylbenzene hydroperoxide as an initiator of oxidation. The temperature of p-cymene was raised to 110°, after which dry air was introduced into it at the rate of 8-10 liters/hr per mole of material. The amount of absorbed oxygen amounted to 0.5-0.6 liters/hr per mole during the initial 4 hrs of oxidation. The content of the hydroperoxide determined iodometrically grew at the rate of 2.7-3% per hour,* which remained constant for 6-7 hrs, then began to decline. After 12 hrs the reaction mixture had accumulated up to 24% of the hydroperoxide.

For the emulsion oxidation there was charged into the reactor 50 ml of p-cymene, 100 ml of 1.3% soda solution, 0.15 g of sodium stearate and a few drops of isopropylbenzene hydroperoxide. The oxidation was run at 95°. The amount of hydroperoxide after 18 hrs was 5.8%.

Isolation of cumyl aldehyde. The oxidized p-cymene (1.38 g) which contained 14.11% of the hydroperoxide, was dissolved in ethyl alcohol and shaken energetically for 4 hrs with excess 40% solution of sodium bisulfite in order to destroy the hydroperoxide.

The aldehyde which was present gave a water soluble compound with the excess sodium bisulfite; the aqueous layer was separated while the hydrocarbon layer was repeatedly treated with sodium bisulfite for a complete removal of the aldehyde. The treatment of the aqueous solution of the bisulfite compound of the aldehyde with 2,4-dinitrophenylhydrazine solution in 2 N hydrochloric acid led to the isolation of a precipitate of a 2,4-dinitrophenylhydrazone. M. p. 236-238° (from xylene). According to data [9]: m. p. 241°.

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* The calculation was made conditionally based on monohydroperoxide.

Found %: C 56.91, 56.92; H 5.17, 5.56; N 16.37. $C_{16}H_{16}O_4N_4$. Calculated %: C 58.53; H 4.94; N 17.06.

A certain divergence from the literature data in the melting point and the analyses, in respect to the carbon and nitrogen content, can be explained probably by the incomplete separation of cumyl aldehyde from the ketone present in the reaction mixture.

Isolation of p-methylacetophenone. From the hydrocarbon layer remaining after the isolation of cumyl aldehyde in the form of its bisulfite compound, there was isolated the p-methylacetophenone in the form of its 2,4-dinitrophenylhydrazone. M. p. 252-253.8°. Mixed melting point gave no depression with an authentic sample.

In the emulsion method of oxidation of p-cymene, there was isolated from the hydrocarbon layer by the same method as above a quantity of the 2,4-dinitrophenylhydrazones of cumyl aldehyde and p-methylacetophenone.

Isolation of cumic acid. p-Cymene (76 g) oxidized in the presence of manganese resinate and containing 14.11% of hydroperoxide, was treated with 5% solution of sodium bicarbonate. After evaporation and acidification of the sodium carbonate extract, there was obtained 0.82 g of cumic acid. M. p. 115° (from water). According to data [9]: m. p. 115-116°.

Isolation of hydroperoxide. Oxidized p-cymene (76 g) containing 14.11% of hydroperoxide was first washed successively with solutions of 5% sodium bicarbonate and 0.5% sodium hydroxide in order to remove acids and phenols, after which it was treated with 15 ml of 5% sodium hydroxide with cooling.

The oxidized p-cymene, after having been washed with water and with alkali, was subjected to a vacuum distillation (6 mm) for the removal of unreacted p-cymene. The residue after the distillation (13.24 g), containing 49.2% of hydroperoxide, was diluted with benzene and treated with 7 ml of 25% sodium hydroxide with cooling. The precipitate of the sodium salt of the hydroperoxide, which formed after standing, was separated, dissolved in water and the solution was saturated with carbon dioxide. The resulting oil was extracted with ether, after the distillation of which there remained 4.91 g of a viscous liquid containing by analysis 75.96% of monohydroperoxide. This liquid was again treated with 25% sodium hydroxide with isolation of the sodium salt of hydroperoxide and isolation of a still more concentrated hydroperoxide. The latter specimen was distilled in vacuo at residual pressure of 10^{-3} mm, which led to the isolation of 1.67 g of a fraction which formed a faintly colored liquid with a penetrating odor.

B. p. 35-38° at 0.001 mm, $n^{20}D$ 1.5199, d_4^{20} 1.0369. MR_D 48.72; calc. 48.82. Found %: C 71.66, 71.68; H 8.79, 8.74; active O 9.11. $C_{10}H_{14}O_2$. Calculated %: C 72.25; H 8.49; active O 9.62.

A sample (1.278 g) of the hydroperoxide was dissolved in 5 ml of ether and this solution was decomposed by a mixture of 5 ml of ether and 10 drops of sulfuric acid (d 1.84). The temperature of the mixture during the decomposition did not rise over 40°. The decomposed mass was neutralized with potassium carbonate and to it was added 10% solution of sodium hydroxide in order to bind p-cresol. Acetone was separated from the cresolate solution by steam distillation and its content in the distillate was determined by the reaction with a solution of hydroxylamine hydrochloride. p-Cresol, remaining in the flask after the distillation of acetone, was determined iodometrically. There was found in the analysis of the decomposed mass (in % of theoretical content): p-cresol 100, acetone 86. p-Cresol was identified in the form of p-cresoxyacetic acid; m. p. 135.5°. According to data [10]: m. p. 136°.

Found %: C 65.34, 65.62; H 6.2, 6.6. $C_9H_{10}O_3$. Calculated %: C 65.04; H 6.06.

Acetone was identified in the form of its 2,4-dinitrophenylhydrazone. M. p. 124-125.3° (from alcohol). According to data [11]: m. p. 126°.

Oxidation of p-sec-butyltoluene. The starting material, p-sec-butyltoluene, was prepared by alkylation of toluene with 2-butene in the presence of 5% of aluminum chloride at 42°. The p-sec-butyltoluene which was isolated by distillation through a laboratory fractionating column, was washed with sulfuric acid (d 1.84), then neutralized with alkali and was again washed with water. It was carefully fractionated after drying.

B. p. 56.5-57° at 4.5 mm, d_4^{20} 0.865, $n^{20}D$ 1.4934. According to data [12]: b. p. 193-194° at 760 mm, d_4^{20} 0.8665, $n^{20}D$ 1.4938.

After oxidation of the resulting butyltoluene with potassium permanganate in alkaline medium there was isolated terephthalic acid, which then was converted to dimethyl terephthalate with m. p. 140° (from alcohol). According to data [13]: m. p. 140°.

Oxidation of p-sec-butyltoluene was run in the presence of 5 mg/mole of manganese resinate at 110° using as oxidation initiator the isopropylbenzene hydroperoxide, as above.

The rate of formation of the hydroperoxide was not over 0.5% per hour* during the first 4 hrs of the process, with a gradual decrease of it in the latter stages of the oxidation. After 16 hrs of oxidation there was accumulated but 4% of the hydroperoxide in the hydrocarbon. The mean rate of oxygen absorption during this process was 0.12-0.14 liter/hr per mole of hydrocarbon during the first 4 hrs of reaction and decreased slightly in the subsequent period of the process. Thus, the major part of the hydroperoxide decomposed during the very process of oxidation. The oxidation of the recovered p-butyltoluene (purified by treatment with sulfuric acid and distillation) was found to proceed at the same rate.

p-sec-Butylbenzaldehyde was isolated from the oxidized hydrocarbon by the technique analogous to that used for the extraction of cumyl aldehyde from oxidized p-cymene, in the form of 2,4-dinitrophenylhydrazone. M. p. 175-177.5° (from alcohol).

Found %: N 16.99. $C_{17}H_{18}O_4N_4$. Calculated %: N 16.35.

p-Methylacetophenone was isolated from the oxidized p-sec-butyltoluene by the method described for the isolation of this substance from oxidized p-cymene, in the form of 2,4-dinitrophenylhydrazone. M. p. 251-252°. A mixed melting point showed no depression.

Isolation of hydroperoxide. Oxidized p-sec-butyltoluene (184 g) containing 3.95% of hydroperoxide was freed of acid admixtures by washing with 5% sodium hydroxide and was then dried. After distillation of the unoxidized butyltoluene in vacuo (54-57° at 5 mm) there remained in the flask a product containing 72.18% of monohydroperoxide. By a series of successive distillations of this substance in vacuo of 0.03 mm in a flask with a low-set side arm, there was obtained 0.8 g of a fraction boiling at 73-75° ($n^{20}D$ 1.5200) showing in iodometric analysis the content of 81.85% of hydroperoxide. A sample (0.7643 g) of the hydroperoxide was dissolved in 5 ml of ether and was decomposed by a mixture of sulfuric acid (d 1.84) and ether. The decomposed mass was neutralized with potassium carbonate and was analyzed for the p-cresol content (see above) and for methyl ethyl ketone content (by the method of acetone determination in decomposition of p-cymene hydroperoxide). The yield (in % of theoretical): p-cresol 100, methyl ethyl ketone 78.7. Methyl ethyl ketone was identified in the form of 2,4-dinitrophenylhydrazone. M. p. 115° (from alcohol). Mixed melting point gave no depression.

Owing to the insignificant amount of p-cresol, we identified it only by a qualitative test [14].

SUMMARY

1. The oxidation of p-cymene and p-sec-butyltoluene by atmospheric oxygen in liquid phase at 110° in the presence of manganese resinate was examined. For p-cymene there was also run an oxidation in aqueous alkaline emulsion at 95°.

2. It was found that in oxidation of p-cymene and p-sec-butyltoluene oxygen reacts with both the primary and the tertiary α-carbon atoms. In case of p-cymene it was established that the direction of the reaction is not changed by alteration of the oxidation method.

3. Hydroperoxide of p-cymene and hydroperoxide of p-sec-butyltoluene were prepared. The isolated hydroperoxides have the structure of tertiary hydroperoxides.

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* Based provisionally on monohydroperoxide.

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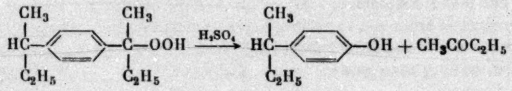
LIQUID PHASE OXIDATION OF ALKAROMATIC HYDROCARBONS BY ATMOSPHERIC OXYGEN

OXIDATION OF p-DI-SEC-BUTYLBENZENE

V. V. Fedorova and P. G. Sergeev

Liquid phase oxidation of dialkyl substituted benzenes in which both substituents are alike had not been studied much up to this time. The exceptions are only p-xylene [1] and m- and p-diisopropylbenzenes [2], from which only monohydroperoxides have been prepared, while the diisopropylbenzenes also yielded the dihydroperoxides. However, even in these cases the kinetics and mechanism of the formation of dihydroperoxides have not been studied. At the same time, the possibility of formation of p- and m-dihydroperoxides by oxidation of such hydrocarbons has not only the scientific but also the practical points of interest as a possible new path for the preparation of hydroquinone and resorcinol.

We conducted a study of the oxidizability of p-di-sec-butylbenzene with atmospheric oxygen in liquid phase at 110° in the presence of minimum amounts of a catalyst which was soluble in the hydrocarbon. The rate of oxidation was 0.22-0.25% of active oxygen per hour. It was found that in the oxidation of this hydrocarbon there are formed both the mono- and the dihydroperoxides. The monohydroperoxide, which was isolated by us in the free state, decomposed under the action of sulfuric acid with formation of p-sec-butylphenol and methyl ethyl ketone by the scheme:



$$\mathrm{CH_3(C_2H_5)HC{-}C_6H_4{-}C(CH_3)(C_2H_5){-}OOH} \xrightarrow{H_2SO_4} \mathrm{CH_3(C_2H_5)HC{-}C_6H_4{-}OH} + \mathrm{CH_3COC_2H_5}$$

The dihydroperoxide, obtained in a mixture with monohydroperoxide, was transformed in the presence of sulfuric acid into hydroquinone and methyl ethyl ketone. For clarification of the practical possibility of preparation of hydroquinone by oxidation of p-di-sec-butylbenzene, we determined the rate of accumulation of the dihydroperoxide in the course of the oxidation.

These determinations were based on the fact that in the reaction of sulfuric acid with peroxide compounds contained in the oxidized p-dibutylbenzene, there are obtained p-butylphenol, hydroquinone and methyl ethyl ketone. By determining the content of these products in the decomposed mass, it was easy to calculate what amounts of mono- and dihydroperoxides were present in the oxidized p-dibutylbenzene prior to the decomposition, Here we neglected, of course, the presence of other products of decomposition of the hydroperoxides, owing to the insignificant amounts of them.

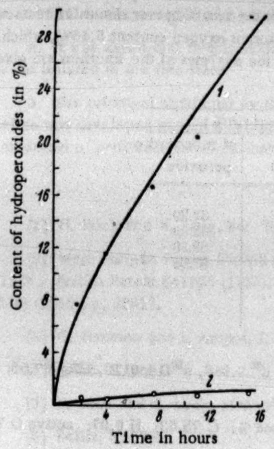
On the basis of data obtained in this manner we constructed the curves of the rates of formation of mono- and dihydroperoxides after a 15-hr oxidation of p-di-sec-butylbenzene.

The form of these curves (see Figure) shows that the rate of formation of the dihydroperoxide is considerably smaller than that of the monohydroperoxide and that, evidently, the dihydroperoxide is formed by oxidation of the monohydroperoxide.

EXPERIMENTAL

Preparation of p-di-sec-butylbenzene. This hydrocarbon was prepared by us by alkylation of benzene with 2-butene in the presence of aluminum chloride (5% of the weight of benzene) at 50-70°. The product isolated by fractionation was purified by being shaken with sulfuric acid (d 1.84) and was washed with alkali and water; after being dried it was distilled.

B. p. 91.5-92° at 3 mm, $n^{20}D$ 1.4878, d_4^{20} 0.8572. According to data [3]: b. p. 240° at 760 mm, $n^{20}D$ 1.4878, d_4^{20} 0.8573.



Accumulation of mono- and dihydroperoxides in oxidation of p-di-sec-butylbenzene: 1) monohydroperoxide; 2) dihydroperoxide.

The structure of the isolated product as that of p-di-sec-butylbenzene was confirmed by its oxidation with potassium permanganate in alkaline medium to terephthalic acid, from which there was then prepared the dimethyl ester with m. p. 140° (from alcohol). According to data [4]: m. p. 140°.

Oxidation was run in a cylindrical glass vessel with a widened portion near the top, provided with a reflux condenser connected to a trap, thermometer, stirrer and a capillary for air inlet. The hydrocarbon with the catalyst dissolved in it (5-7 mg/mole of manganese resinate) and with a few drops of oxidation initiator (hydroperoxide of p-di-sec-butylbenzene containing 5.85% of active oxygen) was heated to 110°, after which air was introduced into it at the rate of 8-10 liters/hr per mole. The mean rate of formation of hydroperoxide was 3-3.5% per hour,* and remained at this level for 12-14 hrs, i. e., the decomposition of the hydroperoxides during the oxidation was quite insignificant and the hydroperoxides themselves were completely stable during the accumulation process. After 14 hrs of oxidation there was accumulated up to 48.5% of hydroperoxide.* The rate of oxygen absorption was 0.6-0.8 liters/hr per mole and also remained constant during the oxidation.

Oxidation of the recovered p-di-sec-butylbenzene obtained by distillation in vacuo from the oxidation products and purified with sulfuric acid proceeded at the same rate as above.

Isolation of dihydroperoxide of p-di-sec-butylbenzene. Oxidized p-di-sec-butylbenzene (103 g) containing 3.53% of active oxygen was washed with 5% soda solution for the removal of acidic products and was distilled in vacuo (2.5 mm) after drying. After the separation of the unoxidized hydrocarbon at 90° there remained in the pot 45.58 g of a liquid containing 6.64% of active oxygen. This residue was diluted with 20 ml of ether and, with cooling, there was added to it 17.5 ml of 40% sodium hydroxide, the addition being made gradually. The resulting precipitate of sodium salts of hydroperoxides was washed with ether by decantation, pressed dry with a spatula in a beaker and was covered with water. Carbon dioxide was passed through the resulting suspension. The hydroperoxides liberated thereby were then extracted with ether, after the distillation of which there remained a viscous liquid containing 9.54% of active oxygen; $n^{20}D$ 1.5243.

Found %: C 68.20, 67.47; H 8.84, 8.71; active O 9.54. $C_{14}H_{22}O_2$. Calculated %: C 75.63; H 9.91; active O 7.20. $C_{14}H_{22}O_4$. Calculated %: C 66.14; H 8.66; active O 12.59.

The presence of the dihydroperoxide in the product was confirmed by the reaction with sulfuric acid.

A small amount of the product (about 2 g) was dissolved in ether and to it was added dropwise a solution of several drops of sulfuric acid (d 1.84) in ether. The temperature of the reaction mixture was kept under 45°. To the decomposed mixture there was added 75 ml of 30% aqueous solution of ferric chloride and the mixture was shaken energetically. Hydroquinone is thereby readily oxidized to benzoquinone [5] which was then extracted with chloroform. For reconversion of benzoquinone back to hydroquinone there was added to the separate chloroform layer 50 ml of 10% sulfuric acid and 65 ml of 10% potassium iodide. The mixture containing the separated iodine was treated with sodium thiosulfate solution. The hydroquinone which is insoluble in chloroform distributed itself in the aqueous layer from which it was then extracted with ether. After the distillation of ether there remained crystals of hydroquinone. The yield was about 0.3 g. M. p. 168-169°. Mixed melting point gave no depression.

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* Calculated provisionally on monohydroperoxide.

Found %: C 65.64, 65.97; H 5.70, 6.17. $C_6H_6O_2$. Calculated %: C 65.44; H 5.49.

Isolation of monohydroperoxide of p-di-sec-butylbenzene. As a result of several experiments on oxidation of p-di-sec-butylbenzene and separation of the dihydroperoxide from the resulting reaction mixture as described above, there was collected a product (total amount of 107.55 g; active oxygen content 5.43%), which was fractionated at the pressure of 0.005 mm. The results of distillation and the analyses of the fractions are given in the Table.

Fraction no.	Boiling point	Wt. of fractions in g	Content (in %)	
			of active oxygen	of monohydroperoxide
1	27—30°	6.48	2.35	32.29
2	37—60.5	28.70	2.37	32.53
3	61—65	14.49	6.49	89.30
4	66—78	26.67	7.10	97.65
Residue	Above 78	21.97	6.2	
Losses		9.24		

The 4th fraction was p-di-sec-butylbenzene monohydroperoxide: d^{20} 0.986, $n^{20}D$ 1.5110, MR_D 67.53; calculated 67.29.

Found %: C 76.21; H 10.25; active O 7.10. $C_{14}H_{22}O_2$. Calculated %: C 75.63; H 9.97; active O 7.20.

It is a rather viscous liquid with a penetrating odor characteristic of peroxides; it does not decompose noticeably on being heated to 110°.

A sample of the monohydroperoxide (9.12 g) was dissolved in ether and decomposed by careful addition of a mixture of sulfuric acid and ether at 45°. The decomposed mixture was neutralized with potassium carbonate and analyzed. For binding the p-butylphenol there was added to the reaction mixture some 10% sodium hydroxide solution, after which the methyl ethyl ketone was separated by steam distillation and was analytically determined in the distillate by its reaction with hydroxylamine hydrochloride. For identification of methyl ethyl ketone its 2,4-dinitrophenylhydrazone was isolated. M. p. 112-113°. Mixed melting point gave no depression.

In the alkaline solution, remaining after the distillation of methyl ethyl ketone, in a separate sample there was iodometrically determined the content of p-sec-butylphenol; from the main body of the solution there was isolated p-sec-butylphenol by acidification; this formed colorless crystals with characteristic odor of freshly tanned leather; m. p. 53°. According to data [6]: m. p. 53-54°.

Found %: C 78.75; H 10.10. $C_{10}H_{14}O$. Calculated %: C 79.90; H 9.39.

In the analysis of the decomposed mass there was found (in % of theoretical): p-sec-butylphenol 99.2 and methyl ethyl ketone 71.2.

Determination of rates of formation of mono- and dihydroperoxides. p-Di-sec-butylbenzene (150 ml) was oxidized under the conditions used by us above. Samples were taken periodically in which the content of active oxygen was determined after which the decomposition of the hydroperoxides with sulfuric acid was performed. The decomposed sample of the reaction mixture was divided into two parts: from one part there were steam distilled, in the presence of sodium bicarbonate solution, the methyl ethyl ketone and the p-sec-butylphenol (hydroquinone remains in the pot under these conditions) and their mixture was separated and analyzed by the method described above as used for the analysis of the products of acidic decomposition of monohydroperoxides.

In the second portion we determined the content of hydroquinone by the method developed for its determination in the presence of resorcinol and other phenols [5].

On the basis of the values of content of p-sec-butylphenol and hydroquinone in the decomposed mixture, as obtained above, we calculated the amounts of mono- and dihydroperoxides present in the oxidized hydrocarbon prior to the decomposition and from these data we constructed the curve of the change of content of hydroperoxides with time.

SUMMARY

1. There was examined the oxidizability of p-di-sec-butylbenzene with atmospheric oxygen in liquid phase at 110° in the presence of a catalyst (manganese resinate, 5-7 mg/mole).

2. It was shown that in this oxidation there are formed mono- and dihydroperoxides; the monohydroperoxide was isolated in the free state.

3. The principal technique for the separate determination of mono- and dihydroperoxidesin the reaction mixture was developed and on this basis there was studied the rate of formation of mono- and dihydroperoxides in oxidation of p-di-sec-butylbenzene.

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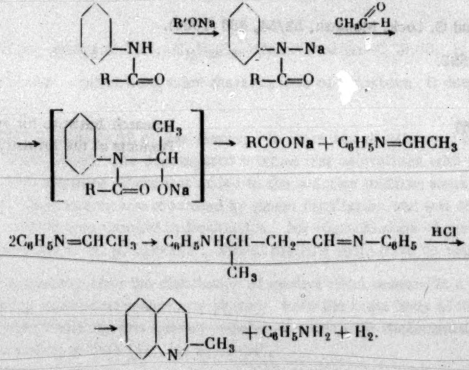
A NEW METHOD FOR THE PREPARATION OF QUINALDINE BASES AND N-ARYLQUINALDINIUM SALTS BY THE CONDENSATION OF ARYLAMINES WITH ALDEHYDES. XX.

V. I. Minkin and B. I. Ardashev

Recent investigations permit the conclusion that the quinaldine synthesis by the method of Doebner and Miller [1] proceeds in two stages: the formation of diethylideneaniline bases (Eibner-Eckstein bases) and their cyclization to quinaldine derivatives [2-9].

The optimum conditions for the formation of the diethylideneaniline bases [7] and for the preparation of the quinaldines from them [8] differ considerably; we therefore made an attempt to separate these stages of the synthesis by condensing acyl anilides with aldehydes in the presence of sodium alcoholate and subsequently cyclizing the products in acid medium. The reaction mechanism basically seems to us to proceed according to the following scheme:

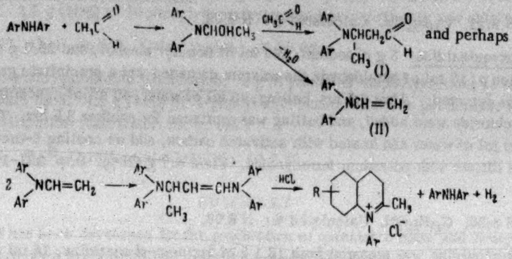

R'ONa
$CH_3C(=O)H$
NH
N—Na
R—C=O
CH_3
N
CH
ONa
$RCOONa + C_6H_5N{=}CHCH_3$
$2C_6H_5N{=}CHCH_3 \rightarrow C_6H_5NHCH(CH_3){-}CH_2{-}CH{=}N{-}C_6H_5$
HCl
N
$-CH_3$
$+ C_6H_5NH_2 + H_2.$

Some quinaldine bases, for example, 6-methoxy-, 6-ethoxy-, and 5,6-benzoquinaldine and others, were obtained in yields amounting to 98% of theoretical calculated on the Eibner-Eckstein base, which was considerably higher than the yields from the methods previously described.

A similar method of carrying out the reaction with separate condensation and cyclization processes can be employed also for the synthesis of the recently described N-arylquinaldinium salts [10-13].

According to the proposed method, a diarylamine is condensed with acetal in nitrobenzene solution, whereupon cyclization is easily obtained just by steam-distilling off the solvent from an acid medium. Thanks to the elimination of the side reaction forming diarylmethane derivatives, which occurs in acid medium [14], and to the presence of an oxidizer, the yield of some of the N-arylquinaldinium derivatives amounts to 40% of the theoretical calculated on the amine taken.

Of the two possible schemes for the main course of the reaction [9]



the first must be excluded, since the Beyer reaction [15] does not go under such conditions.

The production of the dimer of vinyldiphenylamine also is confirmed by the formation of quinaldine from ethylaniline by condensation with acetylene in neutral medium [16] and by the considerable increase in yields of N-arylquinaldinium salts on replacement of acetaldehyde by vinyl ether [17].

EXPERIMENTAL

I. Synthesis of Quinaldine Bases

Formanilide and acetanilide were used for the reaction and gave similar results. Use of the free amine lowered the yield of the quinaldine product approximately by half. As a solvent we used anhydrous ethyl, isobutyl, and isoamyl alcohol, obtaining the best results by the use of isobutyl alcohol.

1. Preparation of 6-methylquinaldine. 3 g of sodium was dissolved in 100 ml of isobutyl alcohol, and 13.5 g of formo-p-toluidide was added with mechanical stirring. The insoluble sodium derivative formed immediately, after which 15 ml of paraldehyde was run in. Moderate boiling of the mixture was continued for 3.5 hrs with constant vigorous stirring. On cooling of the reaction mixture, 40 ml of water, 40 ml of concentrated hydrochloric acid, and 1.5 g of zinc chloride were added and the mixture was kept boiling gently for another 3.5 hrs. The alcohol was steam-distilled off, the residue in the flask was made alkaline, and the base was also steam-distilled. 6-Methylquinaldine was isolated as a complex with potassium ferrocyanide [18] that was decomposed with 10% sodium hydroxide. Yield 7.5 g (48% calculated from the formo-p-toluidide taken, or 96% calculated from the Eibner-Eckstein base). B. p. 118-124° at 2-3 mm, m. p. 58-59°. Picrate, m. p. 187°; methiodide, m. p. 242°.

Found %: N 8.75. $C_{11}H_{11}N$. Calculated %: N 8.92.

2. 6,8-Dimethylquinaldine. 3 g of sodium, 100 ml of isobutyl (or ethyl) alcohol, and 12.1 g of formo-m-xylidide were used. No precipitate of sodium derivative formed. On solution of the formo-m-xylidide, 15 ml of paraldehyde was added, whereupon the solution changed color and a precipitate gradually separated, which was identified qualitatively as sodium formate. The mixture was boiled for 3 hrs, 40-50 ml of solvent was distilled off, 50 ml of water, 50 ml of concentrated hydrochloric acid, and 1.3 g of zinc chloride were added, and boiling was continued for another 3 hrs. 6,8-Dimethylquinaldine was isolated as in Expt. 1. Yield 6.8 g (49%). B. p. 255-270°. Picrate, m. p. 185°.

Found %: N 8.26. $C_{12}H_{13}N$. Calculated %: N 8.19.

3. Quinaldine. 2.8 g of sodium, 100 ml of isoamyl alcohol, 12.1 g of formanilide, and 14 ml of paraldehyde were used. The experiment was similar to Expt. 1. Yield of quinaldine 2.2 g (15%). B. p. 237-250°. Picrate, m. p. 191-192°.

Found %: N 9.90. $C_{10}H_9N$. Calculated %: N 9.79.

4. 6-Methoxyquinaldine. 3 g of sodium, 100 ml of isobutyl alcohol, 15.1 g of formo-p-anisidide, and 17 ml of paraldehyde were used. After 3.5 hrs boiling, 45 ml of concentrated hydrochloric acid was added and

boiling was continued for 1 hr. Yield 6.1 g (35%). B. p. 280-292°, m. p. 64°. Picrate, m. p. 217°; methiodide, m. p. 236-238°; quinophthalone, m. p. 155°.

Found %: N 8.21. $C_{11}H_{11}ON$. Calculated %: N 8.09.

5. 8-Methoxyquinaldine. 3 g of sodium, 100 ml of isobutyl alcohol, and 16.5 g of aceto-o-anisidide were used. Upon addition of 17 ml of paraldehyde the mixture darkened and a precipitate gradually separated, in which sodium acetate was detected. After 4.5 hrs boiling, 40 ml of water, 40 ml of concentrated hydrochloric acid, and 1.5 g of zinc chloride were added, and boiling was continued for another 3.5 hrs. Then the mixture was diluted with 150-200 ml of water and heated with activated carbon, and on cooling 8-methoxyquinaldine was precipitated from the filtrate with potassium ferrocyanide. Yield 4.7 g (28%). B. p. 121-122°. Mercury salt, m. p. 243°.

Found %: N 8.30. $C_{11}H_{11}ON$. Calculated %: N 8.09.

6. 6-Ethoxyquinaldine was prepared from 16.1 g of formo-p-phenetidine, 15 ml of paraldehyde, and 3 g of sodium in 100 ml of isobutyl alcohol after boiling for 4 hrs and then in acid medium for 3 hrs. The isolation was carried out as in Expt. 5. Yield 8.9 g (48%). B. p. 169-175° at 14 mm, m. p. 68°. Picrate, m. p. 193°; methiodide, m. p. 157°.

Found %: N 7.25. $C_{12}H_{13}ON$. Calculated %: N 7.48.

7. 5,6-Benzoquinaldine. 3 g of sodium, 100 ml of isobutyl alcohol, 18.5 g of aceto-β-naphthalide, and 15 ml of paraldehyde were boiled for 7 hrs, and after addition of 40 ml of water, 40 ml of concentrated hydrochloric acid, and 0.5 g of zinc chloride, for 3.5 hrs more. The mixture was diluted to 200 ml and treated with activated carbon. When the filtrate cooled, flakes of the difficultly soluble hydrochloride of 5,6-benzoquinaldine precipitated. Yield of the salt 10.3 g (45%); 5,6-benzoquinaldine was isolated from it by alkalizing. M. p. 79-80°. Picrate, m. p. 228° [19].

Found %: Cl 15.28. $C_{14}H_{12}NCl$. Calculated %: Cl 15.43.

8. 3-Ethyl-6-methylquinaldine. 3 g of sodium, 100 ml of isobutyl alcohol, 13.5 g of formo-p-toluidide, and 24 ml of propionaldehyde were used. The experiment was similar to Expt. 5. Yield 1.8 g (10%). B. p. 284-293°, m. p. 51°. Picrate, m. p. 178°.

Found %: N 7.40. $C_{13}H_{15}N$. Calculated %: N 7.53.

9. N-Phenylquinaldine perchlorate. 16.9 g of diphenylamine was added to a solution of 3 g of sodium in 100 ml of isobutyl alcohol, 15 ml of paraldehyde was added, and the mixture was boiled for 5 hrs. After acidification with 25 ml of concentrated hydrochloric acid, addition of 12 g of o-nitrophenol, and boiling for another 3 hrs, N-phenylquinaldine perchlorate was isolated as in Expt. 10. Yield 3.5 g (11%). B. p. 155-158°.

II. Synthesis of N-Arylquinaldinium Salts

10. N-Phenylquinaldine perchlorate. 16.9 g of diphenylamine, 30 ml of acetal (use of paraldehyde gives almost the same results), and 100 ml of nitrobenzene were boiled gently for 5-6 hrs. 80 ml of concentrated hydrochloric acid was added and the nitrobenzene was slowly steam-distilled off. The unreacted diphenylamine was completely resinified by this treatment and remained on the walls of the flask. The nearly clear solution was poured off, treated with activated carbon, and evaporated to a volume of 50-75 ml, from which N-phenylquinaldine perchlorate was precipitated by the dropwise addition of concentrated perchloric acid. Yield 7 g (22%). M. p. 158-160°. After recrystallization from water m. p. 162-163° (according to [10], m. p. 158-159°; according to [12], 160-162°).

Found %: Cl 11.21. $C_{16}H_{14}O_4NCl$. Calculated %: Cl 11.09.

When the reaction was carried out in nitrobenzene solution and diphenylamine hydrochloride was used instead of the free amine, the yield was lowered to 12-14%.

11. N-p-Tolyl-6-methylquinaldine perchlorate. 9.5 g of di-p-tolylamine, 18 ml of acetal, and 50 ml of nitrobenzene were heated for 5 hrs. 50 ml of concentrated hydrochloric acid was added and the nitrobenzene was steam-distilled off. The further treatment was similar to Expt. 10. Yield 6.7 g (40%). M. p. 188-189°. After recrystallization from aqueous ethanol m. p. 192-193°.

Found %: Cl 10.02. $C_{18}H_{18}O_4NCl$. Calculated %: Cl 9.91.

12. N-Phenylmethylquinaldine perchlorate. 6.9 g of phenyl-p-tolylamine, 15 ml of acetal, and 45 ml of nitrobenzene were used. 3.5 g (28%) of N-phenyl-6-methylquinaldine perchlorate was obtained. M. p. 154-155°.

Found %: Cl 10.77. $C_{17}H_{16}O_4NCl$. Calculated %: Cl 10.63.

13. N-Phenyl-5,6-benzoquinaldine perchlorate. 9 g of phenyl-β-naphthylamine, 13 ml of acetal, and 45 ml of nitrobenzene were used. 6.1 g (40%) of N-phenyl-5,6-benzoquinaldine perchlorate was obtained. M. p. 154-156°. After recrystallization from water, m. p. 160°.

Found %: Cl 9.71. $C_{20}H_{16}O_4NCl$. Calculated %: Cl 9.60.

SUMMARY

1. A new method has been developed for the preparation of quinaldine bases and N-arylquinaldinium salts by the condensation of acylated arylamines and diarylamines with aldehydes.

2. A mechanism has been proposed for these syntheses.

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REACTION OF DIAZO COMPOUNDS WITH SULFAMIC ACID AND ITS DERIVATIVES

XI. CAUSES OF THE COLORATION OF SOME DIAZONIUM AND HETEROCYCLIC AMMONIUM SALTS

D. Z. Zavel'skii and L. A. Lishnevskaia

In previous articles [1-3] we have described the synthesis and properties of diazonium arylsulfamates and acylamidoarylsulfonates and have made some suggestions concerning the causes of the coloration of these salts.

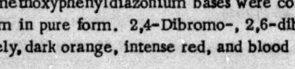
The problem in the present paper is the examination of the colored diazonium salts known in the literature and of compounds related to them and comparison of them with salts synthesized by us for the purpose of ascertaining the reasons for the appearance of color in organic salts of which the cations and anions are colorless.

It is known that diazonium sulfates, nitrates, chlorides, and other diazonium salts in which the anions are colorless are themselves also colorless. However, Hantzsch [4] noted that the bromides, thiocyanates, and iodides of diazo compounds are colored. For example, phenyl-, anisyl-, and pseudocumyldiazonium bromides were almost colorless or light yellow, but mono- and polyhalogenated phenyldiazonium compounds were colored from yellow to red. In this instance, the greater the number of halogen substituents, the deeper was the color and the more explosive the diazo salt. Somewhat more intensely colored and explosive diazo thiocyanates were synthesized by Hirsch [5]. The diazo iodides were especially deeply colored and explosive. The iodides of the strong 2,4,5- and 2,4,6-trimethyl- and 4-methoxyphenyldiazonium bases were colored golden yellow and were so unstable that it was difficult to isolate them in pure form. 2,4-Dibromo-, 2,6-dibromo-, and 2,6-diiodophenyldiazonium iodides were colored, respectively, dark orange, intense red, and blood red and decomposed even in the isolated process.

Thus, in diazonium bromides, thiocyanates, and iodides the depth of color grows with an increase in the electrophilic nature of the substituents in the aryl ring of the diazonium component. A perfectly similar rule is observed for the diazonium acylamidoarylsulfonates and arylsulfamates studied by us, although the extent of deepening of the color in the latter is much greater. The series of salts enumerated have the general property of being colored only in the solid state and yielding colorless or light yellow solutions.

The diazo thiocyanates and iodides are less soluble than the corresponding chlorides. In exactly the same way, the diazonium arylsulfamates and acylamidoarylsulfonates are much less soluble than the corresponding chlorides. It may also be noted that the solubility of the arylsulfamates, as a rule, decreases with an increase in the electrophilic nature of the substituents in the benzene ring of the diazonium component. For example, the 4-chlorophenyldiazonium salt of phenylsulfamic acid dissolves in water to the extent of 7.5%, and the 4-nitrophenyldiazonium salt to the extent of only 3.5%.

To explain the reasons for the coloration and the explosiveness of the diazo bromides, thiocyanates, and iodides in the solid state and their colorlessness in aqueous solution, Hantzsch advanced the suggestion that for these salts as for the diazo cyanides [6] an equilibrium exists between the syn-diazo halide, the diazonium halide, and its ions



$$\begin{matrix}Ar-N\\ \| \\ X-N\end{matrix} \overset{(1)}{\rightleftarrows} \begin{matrix}Ar-N-X\\ ||| \\ N\end{matrix} \overset{(2)}{\rightleftarrows} \begin{matrix}Ar-\overset{+}{N}\\ ||| \\ N\end{matrix} + \overset{-}{X}$$

Syn-diazo halide   Diazonium salt   X=Br, CNS, I

In Hantzsch's opinion, the diazonium salts should be colorless and stable, like ammonium salts with "pentavalent" nitrogen, and the syn-diazo halides should be colored like azo compounds and unstable, even explosive, like the halogen compounds of nitrogen (NCl_3, NBr_3, NI_3). The author thought that the equilibrium (1) between the syn-diazo and the diazonium forms exists in the solid salts, which are solid solutions of the one form in the other, and equilibrium (2) exists in aqueous solutions. In case the diazo group is linked with chlorine, both equilibria are moved to the right (the diazo chlorides are colorless). When chlorine is replaced by bromine, iodine, or a thiocyanate group, the equilibria shift to the left, in the direction of the azo form.

Euler and Hantzsch [7] have shown that movement of the equilibrium to the left is favored not only by the negativity of the substituents and increase in the atomic weight of the halogen, but also by replacement of the water by alcohol (a less dissociated solvent), elevation of the temperature, and decrease in the acidity of the medium. However, Hantzsch did not explain why the presence on the ring in the diazo halides of electronegative substituents (and heavy halogens or thiocyanate as anions) results in a deepening of their color.

Saunders [8], considering the work of Hantzsch, came to the conclusion that ". . . as the basicity of the diazonium diminishes and the acidity of the acid ion decreases, the color of the salts deepens." However, this generalization is in error, since of the three acids whose diazonium salts are colored only thiocyanic acid is comparatively weak (K = 0.14). With regard to hydrobromic and hydriodic acids, they are stronger, not weaker, than hydrochloric acid (0.1 N HCl solution is 92.6% dissociated, HBr 93.5%, and HI 9.50%). However, the depth of coloration of the diazo thiocyanates is between that of the bromides and the iodides. From this it follows that, first, the decrease in the acidity of the anion is not the cause of the coloration of the diazo halides of Hantzsch, and, second, if the diazonium structure is generally admitted for the diazo chlorides, then the diazo bromides and diazo iodides as salts of still stronger acids must be considered diazonium salts also, and not syn-diazo halides.

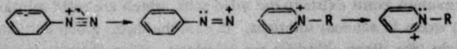
Hantzsch's views on the causes for the coloration of the diazo halides are an essential part of his theory of the structure of the diazo compounds and are usually cited in monographs on the diazo compounds [8, 9]. However, it will be further shown that the coloration of the diazo halides is not caused by a transition to the azo form, but by other factors.

A detailed examination of the literature on the question under consideration has confirmed that all the halides of ammonia and of its alkyl- and simple aryl-substituted derivatives are colorless. An interesting exception is the salts of the nitrogen-containing heterocycles with positively charged tetravalent nitrogen.

In Meyer-Jacobson's handbook [10] it is pointed out that methylquinolinium and methylisoquinolinium iodides are colored bright yellow, while the corresponding cations and anions are colorless. Decker [11] found that methylacridinium chloride is colored yellow, like the cation of this salt, and the iodide is orange-red. Claus [12], Decker [13], and Kaufmann [14], who introduced halogens and nitro groups into the quinolinium nucleus, synthesized the corresponding iodides, which were colored from red to almost black. Kröhnke [15] synthesized a number of iodides, bromides, thiocyanates, and other salts of different pyridinium, quinolinium, and isoquinolinium derivatives, in which the key nitrogen atom was substituted not with methyl, but with a benzyl, phenacyl, or aryl group, whereupon he introduced electrophilic and electron-donor substituents into the ring of the heterocycle, or of the benzyl, phenacyl, or aryl group.

Kröhnke studied in detail the effect of the different substituents and their position on the depth of color of the salts, which he called cycloammonium salts, since they contain an onium nitrogen in the aromatic ring. The author came to the conclusion that the more electrophilic the substituted cycloammonium cation and the more complex the aromatic ring containing the salt-forming nitrogen, the deeper was the color of the salts formed by them. The color of the salts deepened on passing from the bromides to the thiocyanates and from the thiocyanates to the iodides. Upon the solution in water, colored cycloammonium salts were decolorized as a result of dissociation into colorless ions. In solvents with a lower dielectric constant than water the cycloammonium salts decolorized less, or not at all. Heating of the solutions of the colored salts in solvents with a small dielectric constant led to a deepening of the color, and cooling to a weakening of it. Fusion or even simple heating of the solid cycloammonium salts also deepened their color.

Consequently, all the properties of the colored cycloammonium salts are highly similar to the properties of the diazo halides studied by Hantzsch and to those of the arylsulfamates and acylamidoarylsulfonates described by us. At the same time, from an examination of the formula for the diazonium cation and the cycloammonium cation it is apparent that if the former is capable of transition to a diazo cation with trivalent nitrogen (for example, in the formation of azo dyes), then a similar transition for the latter with the formation of a carbonium cation is only slightly probable.



Hence, contrary to Hantzsch's opinion, the color of the diazonium halides and salts of the arylsulfamic and acylamidoarylsulfonic acids must not be related at all to the transition of the diazonium cation to the diazo cation, since in the cycloammonium salts the deepening of color with an increase in the electrophilic nature of the cycloammonium cation and with a rise in the atomic weight of the halide anion occurs in the presence of an indisputable tetravalent salt-forming nitrogen.

Therefore, the cause of the coloration in the compounds examined must be sought in the special nature of the salt bond between the onium nitrogen and the anions of the heavy halides or of some other compounds. For this purpose, it is useful to examine first the behavior of the halide anions in inorganic salts.

As is well known, under the influence of an electric field the electron shell of an ion, especially the outer shell, is deformed more the farther it is from the attracting nucleus. Consequently, the deformation of the iodide or bromide anion under the influence of one and the same cation is considerably greater than that of the chloride or fluoride anion. However, Fajans [16] has already shown that the greater the deformation of the electron shells of the anion and cation, the more the character of the bond between these ions diverges from heteropolar toward homeopolar.

The mutual intrusion of the electron shells of the cation and anion in some salts causes the appearance of color in them. In the table presented below we have collected some data on colored inorganic halides.

From this table it is apparent that the iodides are always more strongly colored than the bromides. Of the ions with one charge, only Ag^+ with an incomplete N electron layer is capable of forming colored salts with the heavy halogens. Of the doubly charged ions, 4 are capable of forming colored salts, and Cu^{2+} with an incomplete M layer forms the darkest and most unstable salts. Among the ions with a triple charge, thallium, which is electronically similar to doubly charged Hg^{2+}, yields halides that are much more deeply colored than the mercury salts. Ti^{4+} and Zr^{4+} with 4 charges, in spite of their small atomic numbers, yield colored iodides. In each of the latter cations the outer electron shell is unfilled.

Summary of Some Data on the Colored Inorganic Halides

Element	Atomic no.	Ion	Completeness of electron layers						Ionic radius	Formulas and colors of salts*	
			K	L	M	N	O	P		iodides	bromides
Ag	47	Ag^+	2	8	18	18			1.13	AgI yellow	$AgBr$ light yellow
Cu	29	Cu^{2+}	2	8	17				0.82	CuI_2 does not exist	$CuBr_2$ brown-black**
Ge	32	Ge^{2+}	2	8	18	2	2		0.98	GeI_2 orange	$GeBr_2$ yellow
Sn	50	Sn^{2+}	2	8	18	18	18		1.02	SnI_2 red	$SnBr_2$ yellow
Hg	80	Hg^{2+}	2	8	18	32	18		1.12	HgI_2 red	$HgBr_2$ colorless
Pb	82	Pb^{2+}	2	8	18	32		2	1.32	PbI_2 yellow	$PbBr_2$ colorless
In	49	In^{3+}	2	8	18	18				InI_3 yellow	$InBr_3$ colorless
Tl	81	Tl^{3+}	2	8	18	32	18		1.05	TlI_3 black	$TlBr_3$ yellow
Ti	22	Ti^{4+}	2	8	8				0.64	TiI_4 dark red	$TiBr_4$ yellow
Zr	40	Zr^{4+}	2	8	18	8			0.87	ZrI_4 brown	$ZrBr_4$-colorless

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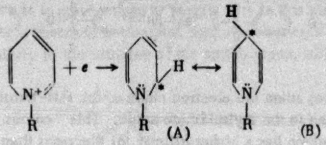
* Color of chlorides not given since they all, except cupric chloride, are colorless.

** The Cu^{2+} ion is colored blue only as the hydrate. In the anhydrous state CuF_2 and $CuSO_4$ are colorless and $CuCl_2$ is dark brown.

Thus, coloration of the inorganic halides is observed in those instances where the electron cloud of a heavy halide ion is greatly deformed by a cation that is capable of creating a powerful electric field, as a result of the fact that it has a small ion radius or several charges. Such salts are much less dissociated in aqueous solutions than the corresponding chlorates and nitrates. If dissociation takes place at all, as in the case of lead iodide, for example, then it is accompanied by decoloration. Additional evidence of the decrease in heteropolarity in the colored halide salts is found in their lower melting and boiling points in comparison with the other corresponding salts.

Decker [11] was the first to point out the similarity of the colored inorganic iodides to the colored ammonium iodides. Meisenheimer [17] explained the coloration of many organic and inorganic iodides by the deformation of the iodide ion by polarizing cations. Kröhnke in his articles [15] analyzed in detail the investigations carried out previously and those that he himself made in the field of the colored cycloammonium salts and expressed the opinion that the phenomenon of bathochromism in salt formation depends not only on the deformation of the anion by the cation, as in the case of AgI, but also on their redox opposition. The author pointed out that Ag$_4$Fe(CN)$_6$, Ag$_2$SO$_3$, and AgS$_2$O$_3$, for example, are colorless, because their anions have a low deformability. However, the salts of these same anions with the cycloammonium cations are deeply colored, since a considerable difference in oxidation-reduction potential exists between such ions.

Kröhnke first suggested that when a colored salt is formed from a cycloammonium cation and an appropriate anion one of the electrons of the anion goes over into the cation, which is thus converted into a radical depicted by structures (A) and (B).



However, the author later was convinced that the pyridinium and quinolinium iodides and ferrocyanides are not paramagnetic and therefore do not contain an unpaired electron. Consequently, he arrived at the conclusion that the electron does not go over completely from the anion to the cation, but "breaks loose" and "hovers" (ist in der Schwebe) in the vicinity of the cation.

Starting with the fact that the diazonium halides contain an onium nitrogen and behave quite like the cycloammonium salts, it is logical to conclude that their color also depends on a special kind of salt bond between the diazonium cation and an easily deformed anion. The diazonium cation actually has strong electron-accepting properties, which can be considerably strengthened by the introduction into the ring of appropriate substituents. In connection with the views of Kröhnke [15] on the oxidizing character of the cycloammonium cations it should be noted that the diazonium cations also have an appreciable oxidizing potential. According to the data of Grachev [18] the oxidizing potential of 4-chlorophenyldiazonium in aqueous solution at pH 2 is +0.86, and that of 4-nitrophenyldiazonium is +0.97 v. Therefore, chlorophenyldiazonium is a stronger oxidizing agent than, for example, Fe^{3+}, the oxidizing potential of which is 0.75 v. Well-known examples of the oxidizing properties of diazonium compounds also are their reactions with alcohol, p-phenylenediamine, arsenous acid, and the like.

In the colored diazonium arylsulfamates of interest to us, which we have shown to have properties similar to those of the diazo iodides and bromides of Hantsch, the arylsulfamate anions occupy the place of the halogens. It must be supposed that these anions apparently also are greatly deformed by the diazonium cations. To explain the reasons for such behavior on the part of the arylsulfamate anions it is of interest to examine the data found in the literature on the diazonium salts of sulfuric acid and some of its derivatives.

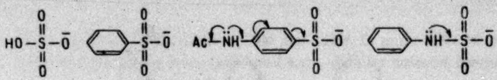
As is well known, the sulfates of the diazo compounds are colorless and extremely easily soluble in water, in which they apparently are completely dissociated. The benzene- and toluenemonosulfonates differ little in color and solubility from the diazonium sulfates. However, the chloro- and nitro-substituted benzene- and toluenesulfonic acids precipitate the less soluble arylsulfonates from solutions of diazonium salts of mineral acids [19]:

$$\mathrm{Ar{-}\overset{+}{N}{\equiv}N]\overline{X} + Ar'{-}SO_3H \longrightarrow Ar{-}\overset{+}{N}{\equiv}N]\overline{O}_3S{-}Ar' + HX}$$

Chloro- and nitro-substituted benzene- and toluenesulfonic acids form colorless salts with diazonium compounds of the benzene series, even those containing chloro or nitro groups. However, with tetraazobenzidine these acids yield salts of a light-yellow or yellow color. In exactly the same way, the diazonium salts of the benzene series form salts with the naphthalenemono- and disulfonic acids that are light-yellow to brownish-yellow in color.

The diazo arylsulfonates, which are characterized by considerably less explosiveness and much greater stability than the chlorides, nitrates, and sulfates, find wide application in dye technology and printing as permanent diazo salts. Apropos of them Saunders [20] writes in his monograph on the diazo compounds that ". . . their stability in the solid state is related, no doubt, to the fact that they are not ionized in this form and is also a result of their high molecular weight."

Still greater stability and depth of color characterize the products of the reaction of diazonium salts with acylamidoarylsulfonic acids that were prepared by Schroeter [21] and further investigated by us [3]. Finally, the diazonium arylsulfamates are quite deeply colored [1, 2]. The reason for the increase in the depth of color of the diazonium salts in passing from the sulfates, through the arylsulfonates and acylamidoarylsulfonates, to the arylsulfamates becomes understandable upon examining the structure of the following anions:

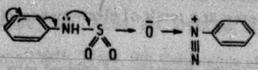


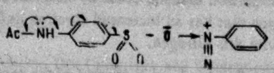
In the bisulfate (or sulfate) anion the electron cloud of the salt-forming oxygen is more stably associated with the central sulfur atom than in the arylsulfonate anion. This comes about because the second salt-forming oxygen in the sulfate ion, which has a higher affinity for electrons than the sulfur (the electronegativity of oxygen is 3.5 ev and that of sulfur is 2.5 ev [22]), draws the electrons away from the latter and makes it more positive and, consequently, more firmly bound with the electrons of the first salt-forming oxygen.

In the arylsulfonate anion the sulfur is linked with a carbon of the phenyl ring, which has the same affinity as the sulfur for electrons; therefore the sulfur becomes less positive and less firmly associated with the electrons of the salt-forming oxygen. Moreover, the phenyl ring promotes, with its sextet of π-electrons, a shift in electron density in a direction dependent on the nature of the substituent [23], in this case the sulfo group. Therefore, when the salt-forming oxygen of the arylsulfonate anion falls under the polarizing influence of a diazonium cation, it is able to give, in addition to an ionic charge, a small part of its electron cloud for greater or less intrusion into the electron gap of the cation. In the final analysis, the heteropolarity of the bond between the cation and the anion decreases, which leads to a decrease in solubility and dissociation of the diazonium arylsulfonate formed in comparison with the corresponding sulfate and in certain cases even results in a slight deepening of the color.

In the acylamidoarylsulfonate anion the nitrogen of the amido group has a pair of solitary electrons, therefore the shift in electron density toward the salt-forming oxygen is naturally more considerable than in the arylsulfonate anion and the intrusion of the electron cloud of the anion into the electron gap of the diazonium cation becomes greater. As a result, the coloration of the diazonium acylamidoacylsulfonates is deeper than that of the arylsulfonates. At the same time it should be noted that the shift of the free electron pair of the amido group in the direction of the sulfo group is partially hindered by the electron-accepting acyl group that is bound with the amido group. The more "acid" the acyl radical, the stronger is the shift in the opposite direction. A hypsochromic effect of corresponding intensity is the result of this. On the other hand, replacement of the phenyl ring by a naphthyl group in the acylamidoarylsulfonate anion leads to a bathochromic effect for the same reasons that this occurs in ordinary dyes.

It can be easily understood that in the arylsulfamate anion the shift of the free pair of electrons of the amido group toward the salt-forming oxygen is considerably greater than in the acylamidoarylsulfonate anion. In this case the mechanism for "pulling" the electron cloud of this oxygen into the electron gap of the diazonium cation is more completely exhibited, as a result of which the diazonium arylsulfamates are more deeply colored than the corresponding acylamidoarylsulfonates.



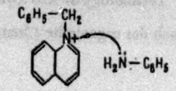


In complete agreement with the above discussion is the fact that the more electron-accepting substituents there are in the phenyl ring, the more considerable is the electron deficiency on the onium nitrogen and, consequently, the deeper is the color of such a diazonium arylsulfamate or acylamidoarylsulfonate.

We think that the phenomenon of bathochromism as a result of salt formation of a special type is rather similar to the phenomena of bathochromism as a result of intermolecular electron interaction of the donor-acceptor type, to which numerous investigators are devoting more and more attention [24, 25]. Of these investigations, the closest to the problem studied by us are the ones concerned with the study of the reaction of dipyridylium and quinolinium salts with amines.

Emmert [26] showed that N,N'-dimethyl-γ,γ'-dipyridylium chloride forms colored molecular compounds with aromatic diamines. Mikhailenko and Minof'ev [27] observed the appearance of color when benzylquinolinium chloride was reacted with monoamines (aniline, p-toluidine, and diphenylamine), but attributed it to the cleavage of the heterocycle with the formation of polymethine dyes. However, Vompe [28] and Izmail'skii [29] showed that in this instance molecular complexes are formed.

In all these cases the quaternary cycloammonium group is considered, like the nitro group, as an acceptor and the arylamine as a donor of electrons [29]. However, in contrast to the nitro group, the quaternary cycloammonium group is a cation. Therefore it is more proper to suggest that in this instance the cation is attracted not to the whole arylamine molecule, as is observed in complex formation between nitro compounds and aromatic hydrocarbons or amines, but particularly to the nitrogen of the amino group, which has an unshared electron pair.



Still more localized is the interaction of a cycloammonium or diazonium cation with an arylsulfamate or acylamidoarylsulfonate anion or with a heavy halide anion. In the crystal lattice of the solid salt formed in this instance the two ions are drawn together, naturally, to a distance usual for an ionic bond. Such a close approach is intensified by the process of partial "pulling in" of the electron cloud from the salt-forming oxygen of the sulfo group by the onium nitrogen, which has an additional electron deficiency because of the electrophilic substituents in the benzene ring. If in this process the density of such an electron cloud is significantly increased because of the electron-donor properties of the amino group, the aryl group, and the substituents on the aryl group, then the salt acquires color. Upon solution of such a colored salt in water it dissociates into ions, which in this case are hydrated. Under these conditions, the more dilute the aqueous solution the more the donor-acceptor mechanism between the cation and anion is disturbed, and the color of the salt is weakened or entirely disappears.

SUMMARY

1. Evidence has been brought forward that the diazo bromides, thiocyanates, and iodides whose color Hantzsch explained on the basis of their syn-diazo structure are actually diazonium salts.

2. The similarity in properties of the diazonium bromides, thiocyanates, and iodides with the diazonium arylsulfamates and acylamidoarylsulfonates has been established.

3. It has been suggested that the arylsulfamate and acylamidoarylsulfonate anions have electron-donor properties that are characteristic also of the bromide, thiocyanate, and iodide anions, and that this general property is the cause of the coloration of the corresponding series of diazonium salts.

4. The similarity of a number of properties of the colored diazonium arylsulfamates, acylamidoarylsulfonates, bromides, thiocyanates, and iodides to the colored bromides, thiocyanates, and iodides of quaternary ammonium bases containing nitrogen in the heterocycle (pyridinium, quinolinium, etc.) has been demonstrated. The

opinion has been expressed that the cause of the color of the series of salts enumerated is the presence in them of an onium nitrogen that has an increased electron deficiency as a result of electron-acceptor substituents in the aryl rings linked with this nitrogen.

5. An explanation has been suggested of the reason for the formation of colored salts from colorless diazonium cations or ammonium cations of nitrogen-containing heterocycles on the one hand, and anions of heavy halides, arylsulfamic and acylamidoarylsulfonic acids on the other hand, as a result of a special donor-acceptor electron interaction between the ions, which supplements the usual salt bond.

6. The similarity and the difference between the donor-acceptor electron interaction of the ions in the colored salts enumerated above and the donor-acceptor interaction of the intermolecular type has been discussed.

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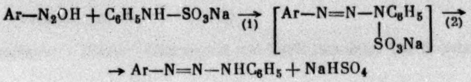
REACTION OF DIAZO COMPOUNDS WITH SULFAMIC ACID AND ITS DERIVATIVES

XII. DIARYLTRIAZENE-N-SULFONIC ACIDS AND THEIR DIAZONIUM SALTS

D. Z. Zavel'skii and L. A. Lishnevskaia

In one of our communications [1] it has been shown that diazo compounds are capable of entering into a diazoamino condensation with phenylsulfamic acid. When this occurred, however, it appeared that the diaryltriazene-N-sulfonates that apparently were formed in the initial phase were capable under the conditions of the diazoamino condensation reaction, i. e., at pH ~ 6 and room temperature, of splitting out their sulfo group and being converted to mixed diaryltriazenes

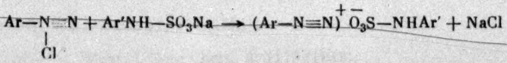


$$Ar{-}N_2OH + C_6H_5NH{-}SO_3Na \xrightarrow[(1)]{} \left[Ar{-}N{=}N{-}\underset{\displaystyle SO_3Na}{\underset{|}{N}}C_6H_5\right] \xrightarrow[(2)]{}$$
$$\rightarrow Ar{-}N{=}N{-}NHC_6H_5 + NaHSO_4$$

In the experiments on diazoamino condensation carried out at that time we aimed for disappearance of the reaction for the active diazo compound, which lasted for a rather long time.

Further investigations have shown that the diazoamino condensation (1) proceeds for not more than 20-30 min, but the reaction of splitting out the sulfo group (2) proceeds considerably more slowly. We were able to utilize this circumstance for the synthesis of the diaryltriazene-N-sulfonates sought and for a study of their interesting properties.

It was established that when a solution of a diazo compound with a pH value of 3 is mixed with a solution of a phenyl- or 4-tolylsulfamate in a buffer of pH 6, during the first moments the brightly colored and rather poorly soluble diazonium salt of the arylsulfamic acid is formed [2].



$$Ar{-}\underset{\underset{Cl}{|}}{N}{=}N + Ar'NH{-}SO_3Na \rightarrow (Ar{-}N{\equiv}N)^{+}\,\overset{-}{O_3}S{-}NHAr' + NaCl \qquad (3)$$

Then in the course of 15-30 min a sharp weakening of the color of the reaction suspension takes place as a result of the conversion of this salt to a new, considerably more highly colored compound, poorly soluble in water and extremely unstable, which proved to be the diaryltriazene-N-sulfonate. When such electrophilically substituted diazo compounds as 2,5-dichloro- or 4-nitrodiazobenzene are used, isolation of the diaryltriazene-N-sulfonates obtained from them requires special precautions to avoid decomposition of the latter. The whole reaction suspension has to be poured in a thin layer onto unfired clay plates.* In this way the mother liquor is quickly drawn off by the pores of the plate and the compound is removed as an almost dry layer, which is additionally dried for a half-hour in vacuo over potassium hydroxide. The compounds obtained are so unstable that the whole process of their synthesis and isolation must not take more than 1 hr. When they are kept even in dry form, their crystalline structure and color rapidly change, and they split out their sulfo group. The diaryltriazene-N-sulfonate obtained from 4-chlorodiazobenzene and phenylsulfamic acid is somewhat more stable. It is possible to isolate it by simple filtration and it can be kept for 1-2 days.

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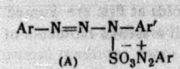
* Before use it is expedient to bake the plates thoroughly and to keep them in a desiccator over some dehydrating agent.

The condensation products of diazo compounds with arylsulfamic acids when exposed in the dry state to the incandescent wire of an electric heater burst into flames instantaneously, and their aqueous suspension combines in neutral medium with any azo components. This forces us to suggest that they contain an active diazo group. However, it further appears that when the new compounds are mixed with an excess of a titrated solution of β-naphthol at pH 7 they actually absorb 1 equivalent of the naphthol in 10 min, but when the reaction is continued further, an additional, much slower absorption of β-naphthol occurs that reaches a maximum of 2 equivalents in 5-6 hrs. Consequently, the compounds under investigation contain two diazo groups, one of which is considerably more active than the other.

The new compound can be dissolved in concentrated hydrochloric acid. If nitrite is added to the hydrochloric acid solution, after a short delay the excess nitrous acid is removed by the addition of sulfamic acid, and after that the mixture is treated with excess β-naphthol at an appropriate pH, then 3 equivalents of β-naphthol are used up in the combination. From this it follows that the molecule of the new compound contains one amino group in addition to the two diazo groups.

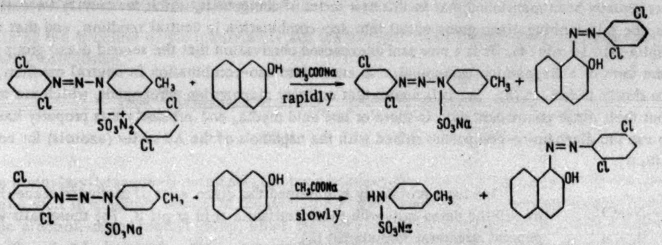


$$\mathrm{Ar{-}N{=}N{-}\underset{\substack{|\;-\;+\\ SO_3N_2Ar}}{N}{-}Ar'}$$

(A)

On the basis of the properties described above we have proposed structure (A) for the new compounds.

Actually, the diazonium salt of the diaryltriazene-N-sulfonic acid has one active salt-forming diazo group and another bound with the imido group of the arylsulfamic acid in a diazoamino compound. Upon coupling with β-naphthol in neutral medium, the condensation product, for example, of 2,5-dichlorodiazobenzene with 4-tolylsulfamic acid, will react in the following way:

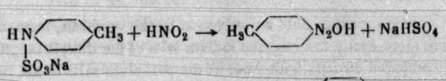


(4)

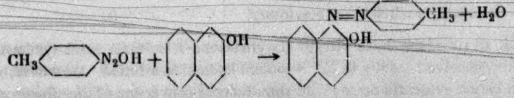
(5)

Investigation has confirmed that a product of both reactions (4) and (5) is 2,5-dichlorophenylazo-β-naphthol, which was isolated and identified with the corresponding specially synthesized azo dye.

It was shown that the solution remaining after coupling of the compound under investigation with β-naphthol in neutral medium and the removal of the azo dye by filtration contains sodium tolylsulfamate, since it absorbs nitrite in acid medium, and after this it couples with β-naphthol to form 4-tolylazo-2-naphthol. The latter was also demonstrated by identification with the same specially synthesized azo dye.

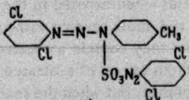


(6)

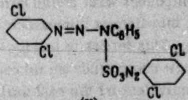


(7)

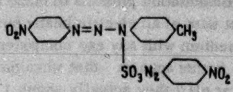
Exactly the same results were obtained in the investigation of the condensation products of 2,5-dichlorodiazobenzene with phenylsulfamic acid and also of 4-nitrodiazobenzene, 3-nitrodiazobenzene, and 4-chlorodiazobenzene with phenyl- and tolylsulfamic acids. The structural formulas of these compounds, which were additionally confirmed by quantitative analyses for diazo nitrogen and sulfur, are given below.



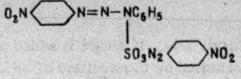
(I)



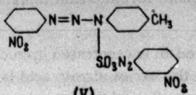
(II)



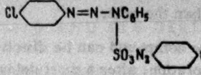
(III)



(IV)

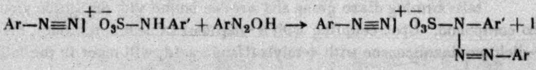


(V)



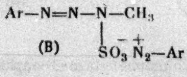
(VI)

Thus it was possible to show that the arylsulfamic acid actually condenses with the diazo compounds to form diaryltriazene-N-sulfonic acids, which precipitate out as diazonium salts as a result of the poor solubility of the latter. In this process, the brightly colored diazonium salts of the arylsulfamic acids at first are formed according to reaction (3), and then these salts enter into a diazoamino condensation with a second molecule of the diazo compound.



$$\mathrm{Ar{-}N{\equiv}N]^{+}\,\overset{-}{O}_3S{-}NHAr' + ArN_2OH \longrightarrow Ar{-}N{\equiv}N]^{+}\,\overset{-}{O}_3S{-}\underset{\displaystyle N{=}N{-}Ar}{\underset{|}{N}}{-}Ar' + H_2O} \qquad (8)$$

It has already been mentioned that in this new series of compounds, which for brevity we call diazoaminodiazo salts, the salt-forming diazo group enters into azo-combination in neutral medium, and that this combination is completed in 10 min (4). It is a new and unexpected observation that the second diazo group, which is bound in the form of a diazoamino compound, also enters into azo-combination in neutral medium, although much more slowly in 5-6 hrs (5). But it is known that ordinary diazoamino compounds, which are soluble in water, can split out their diazo component only in more or less acid media, and precisely this property has made it possible to use the diazoamino compounds mixed with the naphthols of the AS series (azotols) for color printing of fabrics [3, 4].



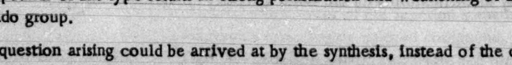
$$\mathrm{Ar{-}N{=}N{-}\underset{\displaystyle \overset{-}{SO_3}\,\overset{+}{N_2}{-}Ar}{\underset{|}{N}}{-}CH_3} \qquad \text{(B)}$$

We have previously synthesized the diazo salts of methyltriazene-N-sulfonic acid by mixing diazo salts with methylsulfamic acid at pH 3. For these salts we proved the general structural formula (B) [5].

However, in these compounds only the salt-forming diazo component was capable of azo-coupling in neutral medium, and the second diazo component, covalently bound with the amino group, was split out only upon acidification. Comparison of the ability of the diazo salts of methylaryltriazene- and diaryltriazenesulfonic acids to couple in neutral medium has compelled us to suggest that either the structural formula proposed by us for the latter is incorrect, or replacement of the methyl group by an aryl group in compounds of this type results in strong polarization and weakening of the bond between the diazo group and the imido group.

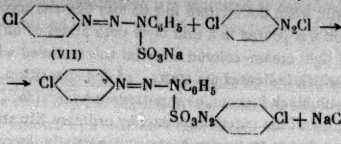
A solution of the question arising could be arrived at by the synthesis, instead of the diazo compounds, of the simpler and therefore more easily investigated sodium salts of the diaryltriazene-N-sulfonic acids, the properties of which could be compared directly with those of the potassium salts of the methylaryltriazene-N-sulfonic acids that have been thoroughly studied by us previously.

It appeared that all six of the diazo salts of diaryltriazene-N-sulfonic acids synthesized by us, which were poorly soluble in water, dissolved readily in 0.1 N sodium hydroxide solution. Moreover, replacement of the diazo cation by the sodium cation evidently occurs with simultaneous conversion of the diazo cation to isodiazotate (in the case of 2,5-dichloro- or 4-nitrodiazobenzene).



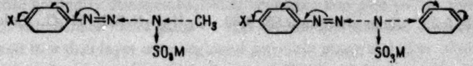
$$\mathrm{Ar{-}N{=}N{-}\underset{\displaystyle SO_3N_2Ar}{\underset{|}{N}}{-}Ar' + NaOH \longrightarrow Ar{-}N{=}N{-}\underset{\displaystyle SO_3Na}{\underset{|}{N}}{-}Ar' + Ar{-}\underset{\displaystyle Na}{\underset{|}{N}}{-}NO} \qquad (9)$$

However, isolation of the sodium salts from the diazoaminodiazo salts synthesized from 2,5-dichloro- or 4-nitrodiazobenzene in a form sufficiently pure for the purposes of the investigation proved to be difficult because of their instability. Only by the action of alkali on the 4-chlorophenyldiazonium salt of 4-chlorodiphenyltriazene-N-sulfonic acid (VI) did we succeed in separating the corresponding sodium salt (VII), the structure of which was exactly established by analyses for diazo nitrogen, sulfur, sodium, and for diazo- and amino-group content, and also by conversion to the original diazoaminodiazo salt (VI) by the action of 4-chlorophenyldiazonium chloride on the sodium salt.



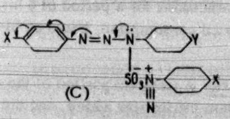
It was confirmed that sodium 4-chlorodiphenyltriazene-N-sulfonate actually is capable of azo-coupling in neutral medium. More than that, it retains the ability to couple in bicarbonate, sodium carbonate, and even caustic alkali medium. Only when the concentration of sodium hydroxide reaches 28-30% does coupling not occur. At the same time, the structurally similar potassium salts of the methylaryltriazene-N-sulfonic acids combine with azo constituents at room temperature only in acid media with pH 2-4 [6]. Consequently, it can be considered clear that just the replacement of the methyl group by an aryl group in these compounds leads to weakening of the bond between the diazo and the amino groups.

Examining the structure of the methylaryl- and the diaryltriazene-N-sulfonates, we apparently can come to the following conclusion.



In the methylaryltriazene-N-sulfonates the bond between the diazo nitrogen and the amino group is weakened as a result of a shift in electron density in the direction of the electrophilic arylazo group and the sulfo group. However, the electron-donor methyl group, which increases the electron density of the imido nitrogen, thus strengthens the bond between the nitrogen and the diazo group. If, however, an aryl group appears in place of the methyl group in the same position, then it, having an electrophilic character, not only does not strengthen, but even weakens the bond of the imido nitrogen with the diazo group.

In our preceding communications [2, 7, 8] we have shown that the diazonium salts of the arylsulfamic acids, in contrast to most of the other diazonium salts, are deeply colored; moreover, the more electrophilic the substituents in the benzene ring of the diazo cation and the more nucleophilic the substituents in the benzene ring of the arylsulfamate anion, the deeper is the color of the salts. The diazonium salts of the diaryltriazene-N-sulfonic acids described in the present work can also be considered as salts of arylsulfamic acids in which a nitrogen has been replaced by an arylazo group (C). Therefore, it might seem that we could expect them also to be deeply and intensely colored. Actually all these salts are colored, weakly or highly, from cream to mustard or light brown.



(C)

The apparent contradiction can be easily explained by the fact that in these salts the imido group of the arylsulfamate ions is replaced by the strongly electrophilic arylazo groups, in which there are also electrophilic substituents (X = NO_2, and the like). As a result of this, the unshared electron pair on the nitrogen of the arylsulfamic acid cannot transmit to the oxygen of the sulfo group the additional electron density necessary to create the special type of salt bond with the diazonium cation that provides the strong bathochromic effect.

EXPERIMENTAL

2,5-Dichlorophenyldiazonium salt of 2,5-dichloro-4'-methyldiphenyltriazene-N-sulfonic acid (I). 1.62 g of 2,5-dichloroaniline was dissolved in 6 ml of 5 N hydrochloric acid, cooled to 0°, and diazotized with a small excess of 5 N nitrite solution. To the diazo solution obtained were added a few crystals of sulfamic acid to remove the excess nitrous acid, and then sodium acetate until a pH of 3 was reached. The solution was filtered and kept in ice.

2.3 g of sodium 4-tolylsulfamate was dissolved in water and 40 ml of concentrated acetate buffer with a pH of 6 was run in. Into the cooled solution, from which the tolylsulfamate began to precipitate, was poured the diazo solution, with stirring at 0°. The reaction suspension immediately became red and in 3-5 min it was filled with red crystals of the 2,5-dichlorophenyldiazonium 4-tolylsulfamate, which upon further stirring began to lose their form and color. In 15-20 min, when the mixture lost its rosy hue and took on a creamy color, stirring was stopped and the reaction suspension was poured in a thin layer onto plates of unfired clay. After remaining on the plates for 40 min the layer of light cream-colored material was removed with a knife. When kept longer, the product began to turn brown, which indicated the start of decomposition. The powder was further dried in a vacuum desiccator painted with black lacquer, over potassium hydroxide. 2.3-2.6 g of the diazonium salt was obtained (80.8-91.3%). Isolation of the reaction product by ordinary filtration and drying, or delay in the process of preparation and isolation, led to its turning brown and partially decomposing.

The diazoaminodiazo salt was extremely unstable on storage. We did not succeed in recrystallizing it, because it was poorly soluble in water and decomposed in organic solvents. However, when the conditions described above were maintained, the product was obtained sufficiently pure for analysis, but the analysis had to be carried out immediately after drying. If the diazoaminodiazo salt was not affected by decomposition, it dissolved completely in the cold in 0.1 N sodium hydroxide solution with a pale yellow coloration. By addition of acetic acid to the alkaline solution the diazoaminodiazo salt could again be precipitated. When the dry product, on the end of a spatula, was brought close to an incandescent electric coil, it immediately burst into flames. The diazoaminodiazo salt that had decomposed on storage gave off sulfuric acid, detectable by the acid reaction to Congo paper and the formation of a precipitate with barium chloride. The suspension of the diazoaminodiazo salt in water actively combined with azo constituents in neutral medium.

Found %: S 5.60, 5.56; diazo nitrogen 9.56, 9.82. $C_{19}H_{13}O_3N_5SCl_4 \cdot 2H_2O$. Calculated %: S 5.63; diazo nitrogen 9.84.

Coupling of diazoaminodiazo salt with β-naphthol in neutral medium. a) 0.5984 g of the compound was stirred with 50 ml of 0.1 N β-naphthol solution at room temperature for 10 min. The β-naphthol solution was previously neutralized with acetic acid to pH 7. The excess β-naphthol was titrated with a 0.1 N p-nitrophenyldiazonium solution immediately after the 10 min combination period.

The actual consumption of 0.1 N β-naphthol solution was 10.88 ml $C_{19}H_{13}O_3N_5SCl_4 \cdot 2H_2O$. The calculated consumption of 0.1 N β-naphthol, based on monoequivalence of the compound, was 10.51 ml.

b) 0.5169 g of the compound was coupled with an excess of β-naphthol under the same conditions, but for a period of 2 hrs. The consumption of 0.1 N β-naphthol solution was 13.28 ml. The calculated consumption based on monoequivalence of the compound, was 9.08 ml.

c) 0.2386 g of the compound was coupled with β-naphthol under similar conditions for a period of 6 hrs. The actual consumption of 0.1 N β-naphthol solution was 8.23 ml. The calculated consumption, based on biequivalence of the compound, was 8.38 ml.

Determination of the total content of two diazo and one amino components. A weighed portion of the diazoaminodiazo salt was dissolved in 50 ml of 0.1 N sodium hydroxide, 0.3 g of sodium nitrite was added, and the solution obtained was poured into a mixture of 5 ml of 5 N hydrochloric acid and ice. After 5 minutes' stirring, 50 ml of 0.1 N β-naphthol solution was run into the solution, its pH was brought to 7 with bicarbonate solution, and after 30 minutes' stirring the excess of β-naphthol was determined with 0.1 N p-nitrophenyldiazonium solution.

0.5431 g of compound required 27.65 ml of 0.1 N β-naphthol. $C_{19}H_{13}O_3N_5SCl_4 \cdot 2H_2O$. Calculated, 28.62 ml of 0.1 N β-naphthol (if the compound is considered triequivalent).

0.4879 g of compound required 26.18 ml of 0.1 N β-naphthol. Calculated, 25.71 ml of 0.1 N β-naphthol.

Qualitative determination of salt-forming diazo compound. 1.3 g of the diazoaminodiazo salt was poured into 50 ml of 0.1 N β-naphthol solution, which had been brought to a pH of 7 with acetic acid, and 100 ml of water and stirred vigorously for 10 min. The red azo dye that separated out was filtered off and the precipitate was washed with warm 0.1 N sodium hydroxide solution, and then with water. After drying and one recrystallization from glacial acetic acid the azo dye melted at 183°. The azo dye specially synthesized from 2,5-dichlorophenyldiazonium and β-naphthol also melted at 183° [9] and when mixed with the dye obtained from the diazoaminodiazo salt it melted without depression.

Qualitative determination of salt-forming diazo components and of the diazo group linked with amino components. 0.8 g of the diazoaminodiazo salt was coupled with β-naphthol at pH 7 for 6 hrs with stirring. After standing overnight, the azo dye that had precipitated was separated as described above. In this case also 2,5-dichlorophenylazo-β-naphthol was obtained with m. p. 183°. Consequently, both azo groups were 2,5-dichlorodiazobenzene groups.

Determination of amino components. 2.0011 g of the diazoaminodiazo salt was coupled with an excess of β-naphthol at pH 7 for 6 hrs. The next day the suspension was acidified and the azo dye that precipitated was filtered off, together with a small amount of β-naphthol that settled out. The filtrate, after addition of 5 ml of concentrated hydrochloric acid, was titrated with 0.1 N nitrite solution. Consumption was 19.36 ml, or 55.1% of the calculated amount.

The solution titrated with nitrite was neutralized with sodium carbonate and poured into an excess of alkaline β-naphthol solution. The azo dye that precipitated was washed with water, dried, and recrystallized twice from glacial acetic acid, after which it melted at 129.0-129.5°. The m. p. of 4-tolylazo-β-naphthol is 130° [9]. Consequently, the amino component was 4-tolylsulfamic acid.

2,5-Dichlorophenyldiazonium salt of 2,5-dichlorodiphenyltriazene-N-sulfonic acid (II). 1.95 g of sodium phenylsulfamate was dissolved in 30 ml of water and mixed with 75 ml of concentrated acetate buffer with pH 6. Then a 0.01 M solution of 2,5-dichlorodiazobenzene prepared as described above was run in with stirring. Immediately a bright orange precipitate of 2,5-dichlorophenyldiazonium phenylsulfamate separated out, which upon further stirring for 30-40 min gradually disappeared, being converted into pale yellow crystals that had the appearance under a microscope of voluminous flakes gathered into rosettes. As soon as the orange crystals disappeared, the reaction mass was poured in a thin layer onto unglazed porcelain plates and after 30-40 minutes' delay the almost dry material was removed with a knife and further dried for 20 min in a vacuum desiccator over solid potassium hydroxide. Yield 2.1-2.3 g (about 80%).

The diazoaminodiazo salt obtained was poorly soluble in water and decomposed in organic solvents. In 0.1 N alkali solution it formed a clear, pale yellow solution that slowly combined with H acid. If the product was not fully soluble in alkali, this was an indication of its partial decomposition.

When the diazoaminodiazo salt was separated by filtration and washing with glacial acetic acid, with subsequent drying on unglazed porcelain, the compound became yellow, then turned brown and was converted into a paste that was acid to Congo, insoluble in water, poorly soluble in sodium hydroxide, and contained the sulfate ion.

The dry diazoaminodiazo salt when brought close to an incandescent electric coil instantly burst into flames.

Found %: diazo nitrogen 9.90. $C_{18}H_{11}O_3N_5SCl_4 \cdot 2H_2O$. Calculated %: diazo nitrogen 10.09.

Determination of total content of diazo components. 0.3203 g of compound was stirred with 20 ml of 5 N hydrochloric acid at 0° for 1 hr. Into the pale yellow, almost transparent, solution that was obtained was poured 25 ml of 0.1 N β-naphthol solution, bicarbonate was added carefully to bring the pH to 7, and, after 30 minutes' stirring, the excess β-naphthol was titrated with 0.1 N solution of p-nitrophenyldiazonium.

Actual consumption of 0.1 N β-naphthol solution was 11.35 ml, calculated 11.54 ml.

Determination of the total of the diazo components and the amino components. 0.1882 g of compound was stirred with 20 ml of 5 N hydrochloric acid at 0° for 1 hr until the material dissolved, an excess of nitrite was added, and after 15 minutes' stirring the excess nitrous acid was removed by the addition of sulfamic acid. The solution of diazo compounds obtained was coupled with an excess of 0.1 N β-naphthol solution, first at pH 7 and finally at pH 9-10.

Actual consumption of 0.1 N β-naphthol solution was 9.97 ml, calculated (based on triequivalence of the compound) 10.17 ml.

4-Nitrophenyldiazonium salt of 4-nitrodiphenyltriazene-N-sulfonic acid (IV). To a solution of 1 g of sodium phenylsulfamate in 25 ml of concentrated acetate buffer with pH 6, cooled in ice, was added 0.005 mmoles of p-nitrophenyldiazonium that had been freed of excess nitrous acid and adjusted to pH 3 with acetate.

Immediately the red-brown 4-nitrophenyldiazonium salt of phenylsulfamic acid precipitated, which upon further stirring gradually started to lose its color and brilliance. When the material was observed under a microscope, it could be seen that there were fine yellow crystals along with the large rose-colored platelets of the diazo salt.

30 min after the start of the reaction the mixture was poured in a thin layer onto unglazed clay plates. In 30-35 min the material was easily poured from the plates as a dry, light brown powder.

The diazoaminodiazo salt was poorly soluble in water, but a suspension combined vigorously with H acid. It was completely soluble in 0.1 N alkali solution, forming a clear red solution. Upon heating over an electric heater the salt instantly burst into flames.

Analysis for the total diazo components and amino components. 0.2509 g of compound was dissolved in 20 ml of 5 N hydrochloric acid cooled with ice. The reddish solution formed was diazotized with an excess of nitrite. In 10 min the excess nitrite was removed by the addition of sulfamic acid and the solution was poured into 25 ml of 0.1 N β-naphthol solution. The pH of the reaction mixture was adjusted to 7 with bicarbonate and the excess β-naphthol was titrated with 0.1 N p-nitrophenyldiazonium solution.

Actual consumption of 0.1 N β-naphthol solution was 15.92 ml, calculated (based on triequivalence of the compound) 15.96 ml.

4-Nitrophenyldiazonium salt of 4-nitro-4'-methyldiphenyltriazenesulfonic acid (III). The diazoaminodiazo salt was prepared from 4-nitrophenyldiazonium and 4-tolylsulfamic acid at pH 6 under conditions similar to those described above. The mustard-colored salt was poorly soluble in water, but a suspension combined vigorously with H acid. It dissolved completely in 0.1 N sodium hydroxide solution with the formation of a clear red solution. It also was soluble in 5 N hydrochloric acid, forming a clear, pale yellowish solution that contained 2 moles of p-nitrodiazobenzene and 1 mole of p-toluidine.

3-Nitrophenyldiazonium salt of 3-nitro-4'-methylphenyltriazene-N-sulfonic acid (V). This compound was prepared under the same conditions as the 4-nitro derivative. The salt was cream-colored. It was poorly soluble in water. An aqueous suspension combined well with azo components. In the dry state, when it was placed on the end of a spatula and brought close to the incandescent coil of an electric heater, it flared up strongly. In 0.1 N alkali it formed a clear yellow solution. It dissolved completely in 5 N hydrochloric acid with the formation of an almost colorless solution containing 2 moles of 3-nitrodiazobenzene and 1 mole of p-toluidine.

4-Chlorophenyldiazonium salt of 4-chlorodiphenyltriazene-N-sulfonic acid (VI). 2.55 g of 4-chloroaniline was diazotized as usual, the excess of nitrous acid was removed with sulfamic acid, and sodium acetate was added to bring the pH to 3. The diazo solution was filtered and kept in ice.

4.3 g of sodium phenylsulfamate was dissolved in 20 ml of water, 30 ml of saturated sodium bicarbonate solution was added, and the mixture was cooled with ice. Into the solution produced was poured a cold solution of 4-chlorophenyldiazonium, with stirring. Thereupon, a light yellow precipitate immediately appeared, but there also was noticeable on the bottom and sides of the reaction beaker a pasty, orange-yellow mass of 4-chlorophenyldiazonium phenylsulfamate, which was gradually converted to a light yellow precipitate on stirring. After 1.5 hrs stirring at 0° the reaction mass, which had become homogeneous, was filtered. The precipitate was washed 5 times with 10-15 ml portions of ice water, transferred to an unglazed porcelain plate, pressed out, and dried overnight in a darkened vacuum desiccator over solid potassium hydroxide. The light yellow powder (fine crystals under the microscope) that was obtained weighed 3.7 g (82.2%). It was poorly soluble in cold water. It dissolved in alcohol and acetone with a yellow color, and was insoluble in benzene and chloroform. The aqueous, alcoholic, and acetone solutions combined with azo components. The solution in acetone deposited in a few minutes a new, weakly colored, flocculent product, which was not investigated.

Found %: diazo nitrogen 12.33; S 6.96. $C_{18}H_{13}O_3N_5SCl_2$. Calculated %: diazo nitrogen 12.44; S 7.12.

Analysis for Combination at pH 7

a) Coupling in 10 min. 0.4522 g of compound: 9.6 ml 0.1 N β-naphthol. $C_{18}H_{13}O_3N_5SCl_2$. Calculated: 10.04 ml 0.1 N β-naphthol solution (if the compound is considered monoequivalent).

b) Coupling in 6 hrs. 0.4778 g compound: 19.9 ml 0.1 N β-naphthol. $C_{18}H_{13}O_3N_5SCl_2$. Calculated: 21.2 ml 0.1 N β-naphthol (if the compound is considered biequivalent).

Sodium salt of 4-chlorodiphenyltriazene-N-sulfonic acid (VII). 2 g of 4-chlorophenyldiazonium salt of 4-chlorophenyltriazene-N-sulfonic acid was dissolved in 40 ml of 0.5 N sodium hydroxide solution at 8°. The compound dissolved almost completely. The filtered orange solution became turbid in the suction flask because the sodium salt started to precipitate. 10 ml of saturated sodium acetate solution was added to the filtrate and it was placed in ice. The precipitate that separated out (light yellow needles under the microscope) was filtered off, washed with several milliliters of ice water, pressed out on an unglazed porcelain plate, and dried in a vacuum desiccator over potassium hydroxide overnight. The dry beige-colored precipitate weighed 0.89 g (54.3%).

The sodium salt of the triazene-N-sulfonic acid was slightly soluble in water (yellow solution). When the aqueous solution stood at room temperature it gradually turned brown, and when heated,it vigorously gave off gas like a solution of an azo compound. The triazene-N-sulfonate solution combined with H acid to form an azo dye not only in acetic acid medium, but also in bicarbonate and sodium carbonate media. The combination still occurred in 0.5 N alkali solution, but ceased in 28-30% solution; however, when bicarbonate was added to the alkali solution, i. e., on conversion to a sodium carbonate medium, combination again was resumed.

The triazene-N-sulfonate was readily soluble in alcohol (the solution was the color of strong tea), and only a little less so in ether (with the same color). The product was slightly soluble in chloroform and insoluble in benzene and petroleum ether.

The dry sodium salt decomposed instantly over an incandescent coil of an electric heater with the evolution of yellow vapors but without fire.

When a solution of 4-chlorophenyldiazonium chloride,neutralized with bicarbonate,was added to an aqueous solution of the sodium salt of 4-chlorodiphenyltriazine-N- sulfonic acid,a light yellow precipitate of the above-described 4-chlorophenyldiazonium 4-chlorodiphenyltriazene-N-sulfonate immediately separated out. When alkali was added to this suspension, a solution of the sodium salt again was formed.

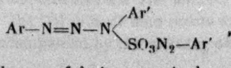
Found %: diazo nitrogen 7.26, 7.43; S 8.47; Na 6.38. $C_{12}H_9O_3N_3SClNa$. Calculated %: diazo nitrogen 7.57; S 8.67; Na 6.22.

Analysis for combination with β-naphthol. 0.4814 g of compound was dissolved in 100 ml of water, 25.0 ml of 0.1 N β-naphthol adjusted to a pH 7 with acetic acid was added, and the mixture was stirred for 2 hrs at room temperature and left overnight. In the morning the excess β-naphthol was titrated with 0.1 N p-nitrophenyldiazonium solution. Consumption of 0.1 N β-naphthol was 13.44 ml; calculated consumption for $C_{12}H_9O_3N_3SClNa$ was 13.02 ml.

Analysis for phenylsulfamic acid. After combination with β-naphthol the precipitate of azo dye was filtered off and washed. To the filtrate and wash water was added 5 ml of concentrated hydrochloric acid and the mixture was titrated with 0.1 N sodium nitrite solution. 13.23 ml was consumed; calculated consumption for $C_{12}H_9O_3N_3SClNa$ was 13.02 ml.

SUMMARY

1. By the action of diazonium salts on arylsulfamic acids, diazonium salts of diaryltriazene-N-sulfonic acids



$\mathrm{Ar{-}N{=}N{-}N}\begin{cases}\mathrm{Ar'}\\ \mathrm{SO_3N_2{-}Ar'}\end{cases}$

, have been synthesized, the structure of the latter salts has been demonstrated, and some of their properties have been studied.

2. It has been established that it is possible to prepare from the diazonium salts of the diaryltriazene-N-sulfonic acids by the action of alkali the corresponding alkali salts, which can again be converted to the starting diazonium salts by exchange decomposition with diazonium chlorides.

3. It has been shown that in contrast to the methylaryltriazene-N-sulfonates and other triazenes of similar structure, in the diaryltriazene-N-sulfonates the diazo component is linked with the imido group so unstably that it is capable of splitting out and combining with azo components in neutral and even in alkaline media. An explanation of this property has been suggested.

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* Original Russian pagination. See C. B. translation.

INVESTIGATIONS IN THE FIELD OF ORGANOCYCLOSILOXANES

III. THE USE OF THE METHOD OF THERMOOXIDATIVE DESTRUCTION FOR THE INVESTIGATION OF THE HYDROLYSIS PRODUCTS OF ALKYLTRICHLOROSILANES

N. N. Sokolov

As a result of the complete hydrolysis of difunctional organosilicon monomers, linear and cyclic organopolysiloxanes are obtained in various ratios. The problem of the structure of polymers formed as a result of the hydrolysis of monomers which are more than difunctional is more complicated.

As a result of the hydrolysis of trifunctional monomers in excess water, complex spatial polymers with the empirical formula $(RSiO_{1.5})_n$ are formed. In this instance the number of blocking groups is markedly reduced and the isolation of the individual hydrolysis products is very difficult.

As a result of the hydrolysis of methyl- and ethyltriethoxysilanes in alcohol it was possible to isolate polymethylsiloxanes with a complex tri- and tetracyclic structure in the amount of several percent from the hydrolyzates [1]. In all these substances the formation of rings is possible owing to the ethoxy or hydroxyl end groups. The most interesting [1] are hexa(ethylsilisesquioxane) $[C_2H_5SiO_{1.5}]_6$, octa(ethylsilisesquioxane) $[C_2H_5SiO_{1.5}]_8$ and the analogous octa(methylsilisesquioxane) [2] which do not contain functional groups.

As a result of the catalytic rearrangement of the hydrolysis products of the corresponding organotrichlorosilanes [3] 1-9% of crystalline cubic octamers of methyl-, ethyl-, N-propyl-, N-butyl and cyclohexylsilisesquioxanes were obtained and cubic silisesquioxane $[Cl_5C_6SiO_{1.5}]_6$ was found [4] in the hydrolysis products of pentachlorophenyltrichlorosilane. Andrianov and Zhdanov [5] put forward the suggestion that internal rings are formed as a result of the hydrolysis of phenyltrichlorosilane.

Cyclic compounds with a "urotropine" structure, where N is replaced by Si, and CH_2 by O were obtained from the hydrolysis products of $RSiCl_3$ (where R = tertiary C_4H_9, iso-C_3H_7) [6].

These data indicate that the hydrolysis of trifunctional monomers is accompanied by the formation of complex ring-shaped structures from which small amounts of the individual substances can be isolated. The main mass of the hydrolyzate does not lend itself to structural analysis, however, because it is an infusible and insoluble gel or powder. It may be assumed, however, that this mass, which is without functional groups, consists mainly of cyclosiloxanes combined in various ways.

We made an attempt to obtain some understanding of the structure of the hydrolysis products of alkyltrichlorosilane by the method of thermooxidative destruction. As was previously shown [7], at temperatures of the order of 200-400° atmospheric oxygen attacks the carbon atom near the silicon in the polymer molecule. As a result, hydroperoxides are first formed; these rapidly break down with the formation of formaldehyde and an OH radical. The OH radical then reacts with the silicon atom giving hydroxy compounds; the condensation of the latter, accompanied by the splitting off of water, leads to the formation of new siloxane bonds in the molecule.

For the thermooxidative destruction the previously synthesized methylchlorocyclosiloxanes [8] of the $[CH_3Si(Cl)O]_{4-7}$ series and ethylchlorocyclosiloxanes of the $[C_2H_5Si(Cl)O]_{3-5}$ series [9] were completely hydrolyzed with the formation of cyclic-stereometric polymers $[RSiO_{1.5}]_n$ with different, but specific, numbers of rings.

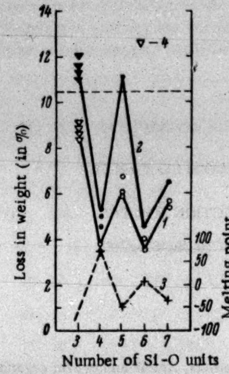

Fig. 1. Thermooxidative destruction of polymethylsiloxanes. 1) 350°, 2 hrs; 2) 400°, 2 hrs; 3) m. p. of methylchlorocyclosiloxanes; 4) data for the polymer from CH_3SiCl_3.

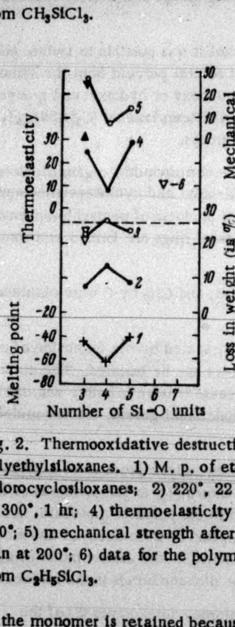

Fig. 2. Thermooxidative destruction of polyethylsiloxanes. 1) M. p. of ethylchlorocyclosiloxanes; 2) 220°, 22 hrs; 3) 300°, 1 hr; 4) thermoelasticity at 150°; 5) mechanical strength after 30 min at 200°; 6) data for the polymer from $C_2H_5SiCl_3$.

Polymers of methyl- and ethyltrichlorosilane were obtained in a similar manner. Figures 1 and 2 give the results of the thermooxidative destruction of these polymers expressed as the loss in weight relative to the number of Si−O units in the ring. The destruction was carried out for 2 hrs at 350 and 400° for polymethylsiloxanes and for 22 hrs (200°) and 1 hr (300°) for polyethylsiloxanes.

The data in Fig. 1 show the clear relationship between the degree of destruction and the number of Si−O units in the polymers; polymethylsiloxanes with an even number of units are destroyed more slowly than similar substances with an odd number of units. This phenomenon is observed at 350°, when the destructive decomposition of the radicals is still not complete, and at 400°, when this decomposition reaches a maximum (the dotted curve in Fig. 1 signifies the theoretical loss in weight corresponding to the disruption of all the radicals). The values of the weight loss for the polymer from methyltrichlorosilane justify the assumption that this polymer is composed of three-unit rings connected by siloxane bonds.

As a check, an analysis was made of the polymers after destruction at 400° (see Table).

Analysis of Polymethylsiloxanes After Thermooxidative Destruction

Polymer	Found		
	H (%)	C (%)	H/C
$[CH_3SiO_{1.5}]_n$	1.48	5.61	3.17
$[CH_3SiO_{1.5}]_{4n}$	3.34	13.35	2.98
$[CH_3SiO_{1.5}]_{5n}$	1.47	5.36	3.30
$[CH_3SiO_{1.5}]_{6n}$	4.46	17.86	2.99
$[CH_3SiO_{1.5}]_{7n}$	4.10	16.10	3.05

Note. Calculated for $CH_3SiO_{1.5}$ %: C 17.9; H 4.48.

The analytical data confirm the fact that maximum destruction occurs with polymers with an odd number of Si−O units. The greater than theoretical weight loss for these polymers with the retention of a certain number of methyl groups is evidently explained by the splitting off of a small amount of volatile products. As we found [7], complete detachment of the radicals does not take place even after heating at 450° for 24 hrs.

From a comparison of Figs. 1 and 3 it is seen that polymethylsiloxanes with an even number of Si−O units undergo the least destruction, i. e., that there is an inverse relationship with the melting points of the corresponding monomers.

In contrast to polymethylsiloxanes, in the case of polyethylsiloxanes (Fig. 2) it was found that polymers with an odd number of Si−O units undergo minimum thermooxidative destruction. In this instance, however, the inverse relationship with the melting points of the monomer is retained because in the case of diethylcyclosiloxanes the "even" polymers have lower melting points than the "odd" ones [13, 14]. The same relationship obtains for ethylchlorocyclosiloxanes (Fig. 2) [9] and, according to our data, for ethylcyclosiloxanes also: triethylcyclotrisiloxane has m. p. of 100°, tetraethylcyclotetrasiloxane, m. p. of 107° and pentaethylcyclopentasiloxane, m. p. of 82°.

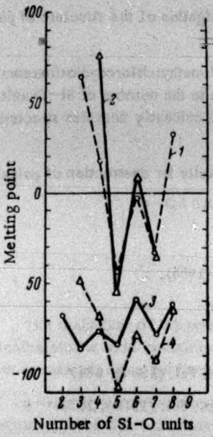

Fig. 3. Melting points. 1) Dimethylcyclosiloxanes [10]; 2) methylchlorocyclosiloxanes [8]; 3) dimethylsiloxanes [12]; 4) methylcylcosiloxanes [8, 11].

The values of the weight losses for the hydrolysis products of ethyltrichlorosilane justify the assumption that this polymer consists mainly of three-unit rings connected by siloxane bonds.

A consideration of the experimental data leads to the conclusion that in this instance a relationship exists between the melting points of the initial monomers and the properties of the corresponding polymers. The "even number factor" (to use the term proposed by V. V. Korshak) embraces a wide range of substances including both those with open chains (e. g., carboxylic acids) and cyclic hydrocarbons (e. g., cycloparaffins). The influence of the even number factor was also established for high-molecular compounds. Korshak and his co-workers [15, 16] found a marked difference in the melting points of polyesters of even-membered and odd-membered dicarboxylic acids: all the polyesters of even-membered dicarboxylic acids melt at higher temperatures, like the "even" acids themselves. The same relationship was established for polyurethanes and polyamides. It is very interesting that carboxylic acids with an even number of carbon atoms have a higher decarboxylation temperature [17].

The presence of the even-number factor is explained by the influence of polar forces between the molecules; with an increase in these forces the packing density of the polymers increases [15, 18] and the polymer must be less subject to thermooxidative reduction, as is seen in the case of polyalkylsiloxanes.

An increase in the packing density must also lead to an increase in the mechanical strength and the thermoelasticity of films of the polymer; this is confirmed by the data of Fig. 2 (curves 4 and 5).

X-rays * showed that the polymer obtained by the hydrolysis of $SiCl_4$ is completely amorphous. Polymethylsiloxane $(CH_3SiO_{1.5})_{4n}$ was found to be amorphous-crystalline. The simultaneous presence of a fine-crystalline and amorphous structure is still more clearly expressed in the case of the polymer $(CH_3SiO_{1.5})_{4n}$. The structure of polyalkylsiloxanes is undoubtedly very complex and is far from showing complete regularity. The conclusion may nevertheless be drawn that a certain number of cyclic trimers exists in the hydrolysis products of CH_3SiCl_3 and $C_2H_4SiCl_3$.

EXPERIMENTAL

Samples of polyalkylsiloxanes were prepared by the hydrolysis of the corresponding monomers dissolved in one volume of toluene. After the samples had been washed free from HCl they were dried for 4 hrs at 120° and crushed. To determine the weight loss as a result of thermooxidative destruction ~ 0.2 g weighed samples of the polymers in open crucibles were placed in a muffle furnace at the given temperature. The hydrolysis and destruction experiments were repeated and gave reproducible results. The intial alkylchlorocyclosiloxanes corresponded to the characteristics found previously [8, 9].

The determination of the thermoelasticity and mechanical strength of the polyethylsiloxanes (directly after hydrolysis they were soluble in toluene) was carried out with lacquer films, 50 μ thick, applied to copper foil, 0.1 mm thick.

The time required for cracks to appear in the film when it was wound around a 3 mm diameter rod served as the criterion of thermoelasticity. The mechanical strength was characterized as the number of reciprocal movements of a 250 g ball along the film in a reversing apparatus up to the moment of perforation of the film as a result of the stress applied to the ball and the copper plate.

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* Taken at our request by K. V. Krylov.

SUMMARY

1. The method of thermooxidative destruction was proposed for the investigation of the structure of polyalkylsiloxanes.

2. It was found that the degree of destruction of the hydrolysis products of methylchlorocyclosiloxanes and ethylchlorocyclosiloxanes is characterized by the even number factor in relation to the number of Si−O units in the initial rings. The hydrolysis products of methyl- and ethyltrichlorosilane are evidently complex structures of cyclic trimers.

3. The hypothesis was advanced that the even number factor and the capacity for destruction of polyalkylsiloxanes depend on the packing density.

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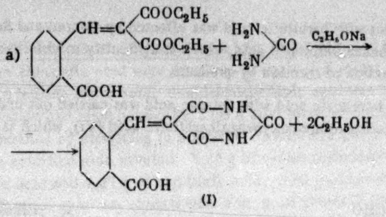
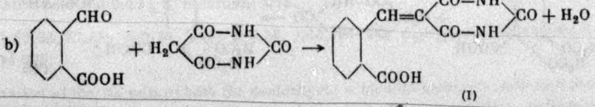
THE SYNTHESIS OF o-CARBOXY- AND o-CARBOXYDIMETHOXYBENZALBARBITURIC ACIDS*

E. I. Chukhina

The main task of the present work was the study of the synthesis of o-carboxy- and o-carboxydimethoxybenzalbarbituric acid containing two acid radicals in the molecule, i. e., o-aldehydebenzoic and opianic acids; these compounds have not been previously described in literature.

o-Carboxybenzalbarbituric acid was synthesized in two ways: a) by the general method of preparing C-substituted barbituric acid from urea and o-carboxybenzylidenemalonic ester [2]; b) by the condensation of o-aldehydebenzoic acid with barbituric acid in an aqueous medium.





o-Carboxybenzalbarbituric acid is a solid crystalline substance with a m. p. of 276-278°. The structure of the compound obtained was established 1) by oxidation, which led to the formation of alloxan and 2) by reduction, as a result of which o-carboxybenzylbarbituric acid (II) was evidently obtained. As a result of the alkaline hydrolysis of this compound o-carboxybenzylmalonic acid (III) was isolated; this compound was first obtained by Wislicenus from phthalylmalonic ester [3] which after being heated is converted to o-carboxyhydrocinnamic acid (IV) (see diagrams at top of next page).

When o-carboxybenzalbarbituric acid was synthesized by the first method (from urea and o-carboxybenzylidenemalonic ester) by-products of the reaction were also obtained: 1) o-carboxycinnamic acid, 2) a crystalline substance of unestablished structure, and 3) a substance with a high nitrogen content which, according to the nitrogen analysis and the value of the gram-equivalent was the diureide of o-carboxybenzylidenemalonic ester (V). (see diagram on following page).

Since a comparatively low yield (45-50%) of the main product was obtained in this reaction the condensation of o-aldehydebenzoic acid with barbituric acid in an aqueous medium was investigated. A similar conden-

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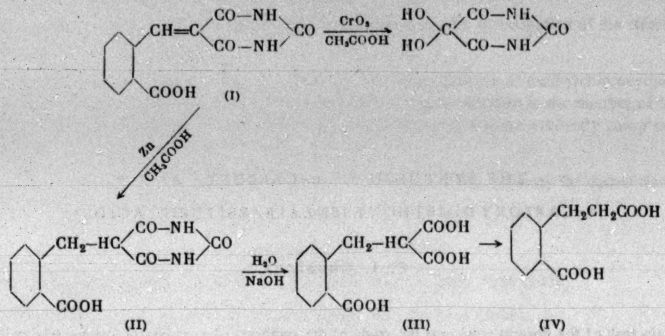
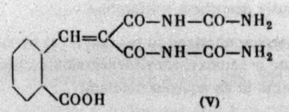
* The present work is the continuation of that commenced together with V. M. Rodionov [1].

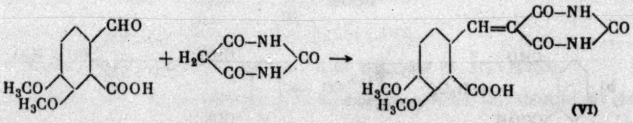




(V)

sation of aromatic aldehydes with barbituric acid was effected by Conrad and Reinbach [4] and other authors [4]. By this method, o-carboxybenzalbarbituric acid, which is difficultly soluble in water, was obtained with a good yield and without the formation of reaction by-products.

The condensation of barbituric acid with opianic acid was carried out under the same conditions; as a result a 75-85% yield of o-carboxydimethoxybenzalbarbituric acid (VI), which is also difficultly soluble in water, was obtained.



(VI)

The synthesis of these two benzal derivatives of barbituric acid with a good yield via the sodium salts of o-aldehyde acids was also found to be possible.

Considerable difficulties were encountered in the determination of the gram-equivalents of the barbituric acid derivatives obtained. The combustion of the Na salts of o-carboxy- and o-carbethoxydimethoxybenzalbarbituric acids in the presence of HNO_3 and H_2SO_4 [5] made it possible to determine the quantitative Na content fairly accurately and to calculate the gram-equivalent of the acid from this.

EXPERIMENTAL

The condensation of o-carboxybenzylidenemalonic ester from urea in the presence of sodium ethylate. When 25 g of o-carboxybenzylidenemalonic ester and 10 g of urea were heated in 40 ml of an alcoholic solution of sodium ethylate (from 4 g of Na) and the mixture was acidified with HCl (1:1), 3 solid fractions were obtained by fractional precipitation*:

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* The precipitates were first treated with ether; o-carboxycinnamic acid was found in the ethereal solutions.

1) 1.96 g of a substance of unidentified structure, in the form of colorless needles with a m. p. of 239-240° (from alcohol);

2) 10.55 g of o-carboxybenzalbarbituric acid in the form of colorless crystals with a m. p. of 276-278°* (from water, with decomp.).

Found %: C 55.60, 55.37; H 2.91, 3.00; N 10.79, 10.82; M 253, 257. $C_{12}H_8O_5N_2$. Calculated %: C 55.39; H 3.08; N 10.88. M 260. **

3) 0.15 g of the diureide of o-carboxybenzylidenemalonic ester in the form of colorless needles (from water) which did not melt up to a temperature of 310-315° and above and was soluble in an aqueous solution of soda.

Found %: N 17.31, 17.43. M 318, 316. $C_{13}H_{12}O_6N_4$. Calculated %: N 17.50. M 320.

When o-carboxybenzalbarbituric acid was oxidized with CrO_3 in glacial acetic acid [2], alloxan was formed. When 0.5 g of o-carboxybenzalbarbituric acid was reduced with zinc dust in CH_3COOH 0.31 g of o-carboxybenzylbarbituric acid was precipitated in the form of colorless needles with a m. p. 236-237° *** (from water).

Found %: N 10.71, 10.80. $C_{12}H_{10}O_5N_2$. Calculated %: N 10.69.

After the alkaline hydrolysis of 0.25 g of o-carboxybenzylbarbituric acid 0.15 g of o-carboxybenzylmalonic acid was obtained in the form of colorless needles with a m. p. of 170-174° (from water; with decomp.).

Found %: C 55.31; H 4.51. $C_{11}H_{10}O_6$. Calculated %: C 55.46; H 4.20.

The o-carboxyhydrocinnamic acid formed by the decarboxylation of the hydrolysis product when heated to 190° showed no depression of the melting point in a mixed melt with o-carboxyhydrocinnamic acid, specially obtained.****

The condensation of o-aldehydebenzoic and opianic acids with barbituric acid in water. Equimolecular amounts of barbituric acid and the aldehydic acid were dissolved in water (0.8 molar solution) by heating in a flask, equipped with a stirrer, on a boiling water bath; o-aldehydebenzoic acid was then added to the solution in small quantities. After the solution had been heated for 3 hrs a precipitate of o-carboxybenzalbarbituric acid was soon precipitated; this was purified by dissolving in a solution of soda and was recrystallized from water after it had been precipitated from the acidified soda solution. 7.00 g of o-carboxybenzalbarbituric acid was obtained from 5.00 g of o-aldehydebenzoic acid and 4.27 g of barbituric acid. 3.60 g of o-carboxydimethoxybenzalbarbituric acid was obtained in the form of colorless crystals with a m. p. of 258-259° (from water; with decomp.) from 2.00 g of opianic acid and 2.19 g of barbituric acid.

Found %: C 52.38, 52.45; H 3.70, 3.80; N 8.56, 8.60. M 319. $C_{14}H_{12}O_7N_2$. Calculated %: C 52.50; H 3.75; N 8.75. M 320.

The condensation of the Na salts of both the o-aldehydic acids with barbituric acid took place under conditions similar to those for the condensation of the acids themselves. The condensation products remained in the aqueous solution and were precipitated on acidification. 8.80 g of o-carboxydimethoxybenzalbarbituric acid was formed from 6.00 g of the Na salt of opianic acid. This acid contains 1 mole of water of crystallization.

Found %: H_2O 5.28. $C_{14}H_{12}O_7N_2 \cdot H_2O$. Calculated %: H_2O 5.32.

The percentage Na content in the samples of the Na salts of both acids which were prepared was determined by the combustion of the substance in the crucible in the presence of H_2SO_4 and HNO_3 [5] and the gram-equivalent of the acid was calculated from it.

The salts of both derivatives of barbituric acid contain 1 mole of water of crystallization.

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* To determine the melting point the capillary containing the substance was lowered into an apparatus heated to 237°.

** The substance was first dried at 110-120°.

*** The capillary containing the substance was lowered into an apparatus heated to 229°.

**** o-Carboxycinnamic acid was prepared by Titley's method [6] and was reduced to o-carboxyhydrocinnamic acid.

Found %: H_2O 5.79. $C_{12}H_7O_5N_2Na \cdot H_2O$. Calculated %: H_2O 6.00.

Found %: Na 7.89; g-equiv. 269. $C_{12}H_7O_5N_2Na$.* Calculated %: Na 8.15; g-equiv. 260.

Found %: Na 6.70; g-equiv. 321. $C_{14}H_{11}O_7N_2Na$. Calculated %: Na 6.73; g-equiv. 320.

SUMMARY

1. It was shown that as a result of the condensation of o-carboxybenzylidenemalonic ester with urea in the presence of sodium alcoholate the main product obtained is o-carboxybenzalbarbituric acid with a yield of 45-50%, calculated on the initial ester. The structure of this compound was established.

2. A simpler method of synthesizing o-carboxy- and o-carboxydimethoxybenzalbarbituric acids by the condensation of o-aldehydic acids or their Na salts with barbituric acid in an aqueous medium with a 75-85% yield was found.

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* The Na content was determined in the dehydrated salts.

** Original Russian pagination. See C. B. translation.

THE SYNTHESIS OF SUBSTANCES WITH A HYPOTENSIVE ACTION – DERIVATIVES OF QUATERNARY AMMONIUM BASES

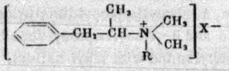
IV. QUATERNARY SALTS OF β-PHENYLISOPROPYLDIMETHYLAMINE

I. B. Simon

It is known that the conversion of the secondary amino group of N-alkylphenylethylamine into a tertiary group and, in particular, the transition to a quaternary ammonium salt modifies the physiological properties of the amine which acts as a depressant instead of a stimulant [1]. For example, according to the data of Alles [2] phenylethyltrimethylammonium hydroxide has a hypotensive action. N-Alkyl derivatives of other analogs of phenylethylamine such as, for example, β-(o-anisyl)-propylmethylamine, or "orthoxin" [3], β-(o-anisyl)-isopropyldimethylamine [3], etc. have a powerful depressant action. It was, therefore, of interest to determine the nature of the influence on the physiological activity of the conversion of the primary amino group in another analog of phenylethylamine – β-phenylisopropylamine (phenamine) – to the corresponding quaternary salts.

For this purpose the quaternary ammonium salts of "phenamine" were synthesized by the treatment of β-phenylisopropyldimethylamine by various alkyl halides.

The Properties of Quaternary Ammonium Salts of β-Phenylisopropylamine



R	X	Molec. wt. of radical	Empirical formula	Melting point	Results of nitrogen analysis* (%)		Depressant activity	Remarks
					found	calc.		
H	Cl	1	$C_{11}H_{18}NCl$	157–158°	—	—	—	White crystals
CH_3	I	15	$C_{12}H_{20}NI$	228–230	4.56, 4.21	4.57	+	Yellowish crystals
C_2H_5	I	29	$C_{13}H_{22}NI$	151	4.08, 3.95	4.38	+	
n-C_3H_7	I	43	$C_{14}H_{24}NI$	188–189	4.26, 4.29	4.20	+	
iso-C_3H_7	I	43	$C_{14}H_{24}NI$	165	4.11, 4.35	4.20	+	White hygroscopic crystals
n-C_4H_9	I	57	$C_{15}H_{26}NI$	113–114	4.02, 3.96	4.04	+	
iso-C_4H_9	I	57	$C_{15}H_{26}NI$	108–110	3.92, 3.74	4.04	+	
iso-C_5H_{11}	I	71	$C_{16}H_{28}NI$	100–102	3.20, 3.26	3.88	++	
C_6H_{11}	I	83	$C_{17}H_{28}NI$	124	3.80, 3.92	3.76	++	White crystals
n.-C_6H_{13}	I	85	$C_{17}H_{30}NI$	77–78	3.89, 3.82	3.73	++	Yellow, very hygroscopic crystals
$C_6H_5CH_2$	Cl	91	$C_{18}H_{24}NCl$	185–187	4.81, 4.35	4.84	+++	White crystals

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* The analyses were carried out in the microanalysis laboratory of our institute.

A list of the quaternary ammonium salts of β-phenylisopropylamine obtained and their properties is given in the table. A comparative investigation of the hypotensive properties of the quaternary ammonium salts of β-phenylisopropylamine was carried out in the School of Pharmacology of the Kharkov Medical Institute (M. S. Kharchenko) in acute experiments on rabbits and cats. From the table it is seen that all the quaternary ammonium salts of β-phenylisopropylamine have a depressant effect which increases with increasing molecular weight of the radical.

EXPERIMENTAL

β-Phenylisopropyldimethylamine. 230 g (5 moles) of 90% formic acid was added with cooling and stirring to 135 g (1 mole) of β-phenylisopropylamine and 200 ml (2.2 mole) of 35% formalin was then added gradually. The mixture was heated on a water bath for 18 hrs and when it had cooled 100 ml of concentrated hydrochloric acid was added. The excess formic acid and formaldehyde were distilled until $^1/_4$ of the contents were left in the distillation flask. The residue was transferred to a separating funnel and 200 ml of 10% caustic soda was added with cooling; the mixture was then extracted several times with ether. The ethereal extract was dried over alkali and distilled. The residue was distilled under vacuum; the b. p. was 115-118° (20 mm). The yield was 120 g (70%). The m. p. of the hydrochloride was 157-158°. According to Woodroof's data [3], β-phenylisopropyldimethylamine has a b. p. of 100° (12 mm), its hydrochloride has a m. p. of 159-161°.

The quaternary salts of β-phenylisopropyldimethylamine. Equimolecular amounts of β-phenylisopropyldimethylamine and the corresponding alkyl halide, dissolved in a small amount of dry benzene, were placed in a small flask, equipped with a reflux condenser. The mixture was heated on a water bath for 3 hrs. The benzene was distilled and the precipitate formed was recrystallized from anhydrous alcohol or dry acetone. The yield of the salts was 60-85%. They were all readily soluble in water, alcohol and acetone and difficultly soluble in ether, benzene, xylene and petroleum ether. The aqueous solutions had a neutral reaction to litmus and were stable at 100°.

SUMMARY

1. β-Phenyl isopropyltrimethylammonium iodide, β-phenylisopropyldimethylethylammonium iodide, β-phenylisopropyldimethylpropylammonium iodide, β-phenylisopropyldimethylbutylammonium iodide, β-phenylisopropyldimethylisobutylammonium iodide, β-phenylisopropyldimethylisoamylammonium iodide, β-phenylisopropyldimethylcyclohexylammonium iodide, β-phenylisopropyldimethylhexylammonium iodide, β-phenyl-, isopropyldimethylbenzylammonium chloride and β-phenylisopropyldimethylisopropylammonium iodide were obtained by treating β-phenylisopropyldimethylamine with alkyl halides.

2. All the quaternary salts obtained have a depressant effect which increases with increasing molecular weight of the radical.

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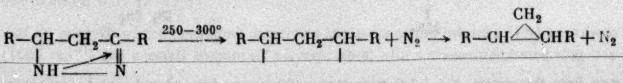
THE REACTIVITY OF α,β-UNSATURATED KETONES AND β-KETONE HALIDES IN THE KIZHNER REACTION

A. P. Meshcheriakov, L. V. Petrova, and Iu. P. Egorov

According to N. M. Kizhner [1, 2], α,β-unsaturated ketones of the type $R-\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}-C=\underset{\displaystyle C}{\underset{|}{C}}-C$ and $R-\underset{\displaystyle O}{\underset{\|}{C}}-CH=C-\underset{\displaystyle C}{\underset{|}{C}}-C$ give pyrazoline bases with hydrazine which decompose during slow distillation only in the presence of a mixture of catalysts (Pt and KOH), liberating nitrogen and forming the corresponding cyclopropane hydrocarbon. It is not necessary, however, to observe this condition in all instances where the pyrazoline base is concerned. For example, in order to obtain cyclopropane hydrocarbons the decomposition of pyrazoline bases was later [3] carried out in the presence of KOH only. The formation of a cyclopropane hydrocarbon as a result of the decomposition of a pyrazoline base during heating can, however, take place in the complete absence of catalysts (both Pt and KOH) at an appropriate temperature, which is somewhat higher than the boiling point of the pyrazoline base.

According to Kizhner [4], the decomposition of the alkylidene hydrazine under the influence of catalytic amounts of KOH precedes its isomerization to the unstable tautomeric form which decomposes with the liberation of nitrogen in a similar manner to aromatic diazo compounds.

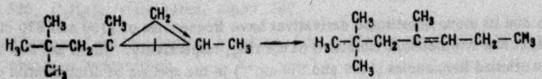
In our opinion the decomposition of the pyrazoline bases can evidently take place via a stage in which a biradical is formed, the latter then giving rise to the cyclopropane hydrocarbon.



$$R-\underset{NH}{\underset{|}{CH}}-CH_2-\underset{N}{\underset{\|}{C}}-R \xrightarrow{250-300^\circ} R-\underset{|}{CH}-CH_2-\underset{|}{CH}-R+N_2 \longrightarrow R-CH\overset{CH_2}{\triangle}CHR+N_2$$

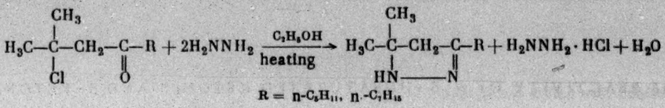
From the mixture of ketones: 4,6,6-trimethyl-3-hepten-2-one and 4,4-dimethyl-3-isopropylidene-2-pentanone we obtained for the first time a mixture of 3,5-dimethyl-5-neopentyl- and 3,5,5-trimethyl-4-tert-butylpyrazolines which on distillation at atmospheric pressure without a catalyst gave a mixture of two isomers: 1,3-dimethyl-3-neopentylcyclopropane and 1,2,2-trimethyl-3-tert-butylcyclopropane. When distilled in the presence of catalysts (Pt and KOH) these pyrazoline bases form a different mixture: 4,6,6-trimethyl-3-heptene and 1,2,2-trimethyl-3-tert-butylcyclopropane (with a predominance of the alkene).

We explain the presence of an alkene in this mixture by the fact that under the influence of KOH and Pt at high temperature the trimethylene ring of 1,3-dimethyl-3-neopentylcyclopropane is broken and 4,6,6-trimethyl-3-heptene is formed.



$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{C}\overset{CH_2}{\triangle}CH-CH_3 \longrightarrow H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{C}=CH-CH_2-CH_3$$

In addition to α,β-unsaturated ketones, β-chloroketones, obtained by the reaction of acid chlorides with alkenes, may be used successfully for obtaining pyrazoline bases [5-7]. When reacted with an alcoholic solution of hydrazine the 2-chloro-2-methyl-4-pentanone and 2-chloro-2-methyl-4-undecanone, which we synthesized by the catalytic method, gave 5,5-dimethyl-3-pentylpyrazoline and 5,5-dimethyl-3-heptylpyrazoline. The reaction takes place according to the following system:



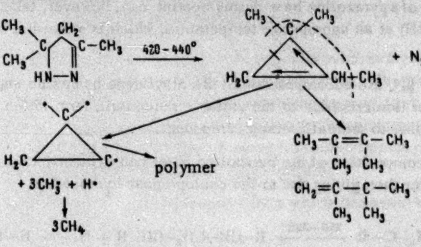
$$H_3C-\underset{Cl}{\overset{CH_3}{C}}-CH_2-\underset{O}{\overset{}{\underset{\|}{C}}}-R+2H_2NNH_2\xrightarrow[\text{heating}]{C_2H_5OH}H_3C-\underset{HN}{\overset{CH_3}{C}}-CH_2-\underset{\underset{N}{\|}}{C}-R+H_2NNH_2\cdot HCl+H_2O$$

$R = n\text{-}C_5H_{11},\ n\text{-}C_7H_{15}$

On slow distillation in the presence of Pt or KOH the above-mentioned pyrazoline bases gave 1,1-dimethyl-N-amylcyclopropane and 1,1-dimethyl-N-heptylcyclopropane. When these pyrazoline bases were heated to constant boiling at atmospheric pressure in the presence of a catalyst the same hydrocarbons were formed.

Since the pyrazoline bases which we investigated have relatively high boiling points (the boiling points of these compounds at atmospheric pressure are above 200°) at which they already decompose into nitrogen and a cyclopropane hydrocarbon, it was suggested that the low-boiling pyrazoline would also decompose without a catalyst (Pt and KOH) at increased temperature, with the formation of cyclopropane hydrocarbons.

We carried out experiments on the thermal decomposition of 3,5,5-trimethylpyrazoline at 420-440°. The data of the gas analysis indicated that when the base decomposes,1 molecule of nitrogen is liberated from 1 molecule of the latter and 3 molecules of methane are formed; in addition, a mixture of alkenes, in which tetramethylethylene predominates, is formed. On the basis of these data it may be assumed that the decomposition of the pyrazoline base takes place according to the following system:



As may be seen from the system, the 1,1,2-trimethylcyclopropane formed under high-temperature conditions is mainly demethylated and gives methane while in the molecules of the cyclopropane hydrocarbon (of which a small amount remains) the ring is is broken and a mixture of alkenes with a predominance of tetramethylethylene is formed.

In addition to chemical methods we used the combined dispersion spectrum method for proving the structure of the cyclopropane hydrocarbons obtained.

The combined dispersion spectra of cyclopropane compounds are still insufficiently studied [8-11]. In the combined dispersion spectra of trimethylene compounds several characteristic frequencies were, however, established [12], from which it was possible to judge the presence of a three-membered ring in these compounds. Among the frequencies of this type there are frequencies in the 3000-3100 cm^{-1} region which correspond to the vibrations of the C—H bond of the ring.

Cyclopropane and its mono-substituted derivatives have frequencies of 1190 and 870 cm^{-1} which correspond to the antisymmetrical and symmetrical vibrations of the ring, respectively. There are 3-4 frequencies instead of the two above-mentioned frequencies (1190 and 870 cm^{-1}) in the spectra of disubstituted cyclopropanes.

Only two spectra of cyclopropane compounds with a quaternary carbon atom are given in the literature, i. e., 1,1-dimethylcyclopropane and 1,1,2-trimethylcyclopropane [9, 10]. In the spectra of these compounds there are also lines in the above-mentioned regions, indicating the presence of a three-membered ring. In addition, there is also a fairly intense line with a frequency of ~ 678 cm^{-1}. This frequency is evidently characteristic for a gem-substituted carbon atom in the ring (average frequency 706 cm^{-1} in the spectrum of 1,1-dimethylcyclohexane [10]).

EXPERIMENTAL

The preparation and decomposition of 3,5-dimethyl-5-neopentyl- and 3,5,5-trimethyl-4-tert -butylpyrazolines. A mixture of ketones was used to obtain the given pyrazolines: 4,6,6-trimethyl-3-penten-2-one and 4,4-dimethyl-3-isopropylidene-2-pentanone, synthesized from Butlerov's diisobutylene (80% 2,2,4-trimethyl-4-pentene and 20% 2,2,4-trimethyl-3-pentene) by Kondakov's method [5]. The first isomer is predominant in this mixture of ketones.

B. p. 65-68° (1-2 mm), d_4^{20} 0.8419, $n^{20}D$ 1.4467, MR_D 48.079; calc. 47.927. Found %: C 77.35; H 11.57. $C_{10}H_{18}O$. Calculated %: C 77.71; H 11.70.

The 2,4-dinitrophenylhydrazone with a m. p. of 159-160° (from ethyl alcohol) was obtained.

Found %: N 16.77. $C_{16}H_{22}O_4N_4$. Calculated %: N 16.76.

The pyrazoline base was obtained by boiling an alcoholic solution of the hydrazine hydrate for 6 hrs with an alcoholic solution of the mixture of ketones obtained. 41.0 g (72.2%) of pyrazoline base was obtained from 61 g of the mixture of ketones and 41 g of hydrazine hydrate. Taking the structure of the initial ketones into consideration it must be assumed that the base is a mixture of 3,5-dimethyl-5-neopentyl- and 3,5,5-trimethyl-4-tert - butylpyrazolines with a predominance of the first isomer.

The base was decomposed in a small copper flask, equipped with a fir-tree shaped fractionating column, connected to a horizontal condenser. 8-10 g of KOH, a catalytic quantity of 5% platinum on charcoal and 48 g of the mixture of isomeric pyrazolines were placed in the flask. The decomposition products were distilled at 128-139°. The hydrocarbons were separated from the undecomposed base in a column (with an efficiency of 18 theoretical plates), washed free from traces of base with 50% CH_3COOH, then washed with a 25% NaOH solution and water, dried with $CaCl_2$ and distilled twice over Na in acolumn. 24 g (50%) of a mixture of hydrocarbons was obtained.

B. p. 144-145°, d_4^{20} 0.7496, $n^{20}D$ 1.4243, MR_D 47.48; calc. 46.18. The exaltation of 1.3 characterizes the presence of one double bond.

On the basis of an analysis of the combined dispersion spectrum of the mixture of hydrocarbons the presence of a double bond (1663 cm^{-1}) and a small amount of a hydrocarbon with a three-membered ring was established.

The product of the catalytic decomposition of pyrazolines, therefore, consists mainly of an alkene and a small amount of a hydrocarbon with a trimethylene ring.

The structure of the alkene obtained (2,2,4-trimethyl-4-heptene) was established by oxidizing it with a 1% solution of $KMnO_4$. The following oxidation products were isolated.

a) Methyl neopentyl ketone with a b. p. of 126-130°. Its semicarbazone with a m. p. of 123-125° was obtained; literature data: m. p. 124° [13].

Found %: N 24.83. $C_8H_{17}ON_3$. Calculated %: N 24.56.

b) Propionic acid with a b. p. of 141-145°. It was identified from its acid equivalent by titrating with 0.1 N NaOH.

Found: equiv. 520. $C_3H_6O_2$. Calculated: equiv. 540.

By repeated distillation of the low-boiling fractions of the oxidation products containing ketone it was possible to isolate a cyclopropane hydrocarbon.

B. p. 144-145°, d_4^{20} 0.7575, $n^{20}D$ 1.4250, MR_D 47.04; calc. 46.18. Exaltation 0.8 due to a three-membered ring. Found %: C 85.68; H 14.33. $C_{10}H_{20}$. Calculated %: C 85.63; H 14.37.

*Combined dispersion spectrum,** $\Delta\gamma$ cm^{-1}: 220 (9), 320 (9), 463 (9), 636 (0), 702 (2), 720 (1), 767 (1), 799 (1), 1109 (2), 1200 (0), 1409 (1), 1447 (1), 2868 (1), 2910 (5), 2921 (1), 2964 (1), 2995 (1).

After the removal of the alkene (by oxidation with a 1% solution of $KMnO_4$) we were, therefore, left with only 1,2,2-trimethyl-3-tert -butylcyclopropane.

In another experiment a mixture of 3,5-dimethyl-5-neopentyl- and 3,5,5-trimethyl-4-tert -butylpyrazolines was distilled at atmospheric pressure. The distillation temperature of the hydrocarbons was 120-140°. A hydrocarbon was isolated with a yield of 10% after the mixture had been distilled twice over Na.

B. p. 144-145°, d_4^{20} 0.7559, $n^{20}D$ 1.4213, MR_D 46.94; calc. 46.18. The exaltation of 0.76 characterizes a three-membered ring.

Combined dispersion spectrum, $\Delta\gamma$ cm^{-1}: 528 (1b), 688 (0), 714 (4), 748 (3b), 775 (2b), 825 (0), 853 (1), 884 (1), 910 (1), 933 (2), 980 (0), 1098 (3b), 1162 (0), 1202 (2), 1245 (3b), 1366 (1), 1392 (0), 1445 (4b), 1461 (1), 1642 (0), 1662 (0), 2870 (5b), 2902 (3b), 2956 (8b), 2988 (2).

In addition to the frequencies characteristic for a gem-substituted three-membered ring (714 and 2988 cm^{-1}) frequencies of the C=C bonds (1642 and 1662 cm^{-1}) were detected. The intensity of these lines denotes only a small admixture of alkenes.

We also carried out observations on the stability of a mixture of bases at room temperature in the presence of KOH, K_2CO_3, Al_2O_3 and $Ba(OH)_2$ over a period of 3 days. When allowed to stand in light these bases decompose appreciably in the presence of KOH and K_2CO_3 from the first moment of contact (liberation of nitrogen). In the presence of Al_2O_3 and $Ba(OH)_2$ the decomposition process is very sluggish.

The synthesis of 2-chloro-2-methyl-4-nonanone. To obtain 1,1-dimethyl-2-pentylcyclopropane we synthesized 2-chloro-2-methyl-4-nonanone from capronyl chloride and isobutylene in the presence of 10% $ZnCl_2$. The capronyl chloride had the following properties: b. p. 65-70° (45-50 mm), d_4^{20} 1.0416 (literature data: b. p. 150-153° [14]). The synthesis of 2-chloro-2-methyl-4-nonanone was carried out in a metal boat at room temperature with constant shaking on a rocker for 18 hrs. The isobutylene was added to the boat in liquid form. 238 g (97.5%) of crude 2-chloro-2-methyl-4-nonanone was obtained from 172 g of the acyl chloride and 120 g of isobutylene. Two fractions were obtained by distilling it under vacuum: 1st fraction, b. p. 78-90° (2 mm), d_4^{20} 0.8896, $n^{20}D$ 1.4480, 58 g; 2nd, b. p. 90-95° (2 mm), d_4^{20} 0.8782, $n^{20}D$ 1.4538, 62.5 g.

Since, as was repeatedly noted, HCl is split off during the process of distillation of the chloroketone, the 1st fraction, which consisted mainly of an unsaturated ketone with the composition $C_{10}H_{18}O$, contained 2-chloro-2-methyl-4-nonanone as an admixture. The 2nd fraction was mainly 2-chloro-2-methyl-4-nonane.

To obtain 2-methyl-2-nonen-4-one in the pure form the 1st fraction was treated with a saturated solution of K_2CO_3 by boiling on a water bath for 6 hrs. Since the ketone still contained traces of chlorine it was washed with a saturated solution of soda, then with water and was finally dried with $CaCl_2$. A 62.6% yield of 2-methyl-2-nonen-4-one was obtained by distillation.

B. p. 205-207°, d_4^{20} 0.8524, $n^{20}D$ 1.4522, MR_D 48.57; calc. 47.92. Found %: C 76.90; H 11.61. $C_{10}H_{18}O$. Calculated %: C 77.90; H 11.68. (The discrepancy in the analysis evidently results from the residual traces of chlorine.)

The semicarbazone of 2-methyl-2-nonen-4-one with a m. p. of 79-80° (from 50% C_2H_5OH) was obtained.

Found %: N 21.12. $C_{11}H_{21}ON_3$. Calculated %: N 21.32.

The preparation of 3-pentyl-5,5-dimethylpyrazoline. 31 g of 2-chloro-2-methyl-4-nonanone and an alcoholic solution containing 8.2 g of hydrazine hydrate were taken for the reaction. When they were mixed heat was evolved and the temperature rose to 60-65°. The mixture was subsequently boiled with constant stirring for 6 hrs. After the alcohol and unreacted hydrazine hydrate had been distilled off the reaction product was dried with KOH and distilled. The yield of 3-pentyl-5,5-dimethylpyrazoline was 97.4%.

B. p. 215-220° (765 mm), d_4^{20} 0.8797, $n^{20}D$ 1.4580, MR_D 51.57; calc. 51.35.

The catalytic decomposition of 3-pentyl-5,5-dimethylpyrazoline. As indicated above, the decomposition of the pyrazoline base(26.5) was carried out in the presence of 10 g of KOH and a catalytic quantity of 5% platinum on charcoal. The hydrocarbon was distilled at 128-170°, washed with 50% CH_3COOH (to remove traces of base), neutralized with a 25% NaOH solution, washed with water and dried with $CaCl_2$. A 66.0% yield of 1,1-dimethyl-2-N-pentylcyclopropane was obtained by distilling the treated hydrocarbon twice over Na in a column with an efficiency of 18 theoretical plates.

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* The spectrum of this compound is incomplete.

B. p. 156.5-157° (740 mm), d_4^{20} 0.7520, $n^{20}D$ 1.4205, MR_D 47.06; calc. 46.18. Exaltation due to a three-membered ring 0.88. Found %: C 85.62; H 14.50. $C_{10}H_{20}$. Calculated %: C 85.63; H 14.37.

Combined dispersion spectrum, $\Delta\gamma$ cm^{-1}: 371 (2), 687 (8), 756 (0), 790 (0), 866 (2), 905 (0), 960 (0), 1025 (1), 1076 (0), 1112 (3b), 1130 (3), 1178 (1), 1224 (1), 1307 (7), 1397 (2), 1440 (10), 1450 (9), 1460 (9), 2852 (1), 2892 (3), 2937 (4), 2990) (4).

We obtained the same hydrocarbon by the slow distillation of 3-pentyl-5,5-dimethylpyrazoline.

B. p. 156-157°, d_4^{20} 0.7514, $n^{20}D$ 1.4205, MR_D 47.16; calc. 46.18.

The synthesis of 2-chloro-2-methyl-4-undecanone. The synthesis was carried out under conditions similar to those for the synthesis of 2-chloro-2-methyl-4-nonanone (see above) from capryl chloride and isobutylene. The boiling point of the capryl chloride was 85-95° (10 mm); literature data: b. p. 194-195° [15]. 292 g (97.7%) of 2-chloro-2-methyl-4-undecanone was obtained from 222 g of capryl chloride and 77 g of isobutylene. 152 g of the chloroketone was distilled under vacuum; two fractions were isolated: 1st, b. p. 87-110° (1 mm), 40 g; 2nd, b. p. 100-115° (1 mm) 62 g.

The 2nd fraction was 2-chloro-2-methyl-4-undecanone, $C_{12}H_{23}OCl$, d_4^{20} 0.8861, $n^{20}D$ 1.4581.

The 1st fraction which consisted mainly of the ketone $C_{12}H_{22}O$ contained an admixture of the chloroketone $C_{12}H_{23}OCl$. The ketone $C_{12}H_{22}O$ was obtained with a yield of 55% by boiling the 1st fraction with a saturated solution of K_2CO_3.

B. p. 230-235°, d_4^{20} 0.8495, $n^{20}D$ 1.4510, MR_D 57.68; calc. 57.16. Found %: C 78.10; H 11.95. $C_{12}H_{22}O$. Calculated %: C 77.94; H 12.08.

The semicarbazone with a m. p. of 94-95° (from C_2H_5OH) was obtained.

Found %: N 17.68. $C_{13}H_{25}ON_3$. Calculated %: N 17.55.

The preparation of 3-heptyl-5,5-dimethylpyrazoline. The reaction was carried out under the conditions described above. 70 g of 2-chloro-2-methyl-4-undecanone in 40 ml of C_2H_5OH and 24 g of hydrazine hydrate in 40 ml of C_2H_5OH were taken. The reaction product was treated in the same way as in the previous experiments. 44 g (70%) of 3-heptyl-5,5-dimethylpyrazoline was obtained by distillation. On standing, the pyrazoline decomposed with the evolution of nitrogen.

B. p. 118-122° (1 mm), d_4^{20} 0.7803, $n^{20}D$ 1.4613, MR_D 61.776; calc. 61.694.

The catalytic decomposition of 3-heptyl-5,5-dimethylpyrazoline. The decomposition was carried out in a small copper flask in the presence of dry KOH and traces of 5% platinum on charcoal. 44 g of pyrazoline was used for the decomposition. The hydrocarbon distilled at 172-205°. The decomposition product of the base was treated in a similar manner to the previous experiments. 14.5 g (66.8%) of 1,1-dimethyl-2-heptylcyclopropane was obtained.

B. p. 200-201°, d_4^{20} 0.7675, $n^{20}D$ 1.4278, MR_D 56.06; calc. 55.41. The exaltation of 0.65 characterizes the presence of a three-membered ring in the hydrocarbon.

The analysis of the combined dispersion spectrum of the hydrocarbon indicated the presence of 95% of a hydrocarbon with a three-membered ring and approximately 5% alkene. The alkene was removed by oxidizing the hydrocarbon with a 1% solution of $KMnO_4$; 1,1-dimethyl-2-N-heptylcyclopropane remained.

B. p. 200-201°, d_4^{20}, 0.7681, $n^{20}D$ 1.4285, MR_D 56.14; calc. 55.41. The exaltation of 0.73 characterizes the presence of a three-membered ring. Found %: C 85.60; H 14.42. $C_{12}H_{24}$. Calculated %: C 85.63; H 14.37.

Combined dispersion spectrum, $\Delta\gamma$ cm^{-1}: 367 (3), 585 (0), 627 (1), 683 (10), 768 (0), 864 (3), 893 (2), 952 (2), 1000 (1), 1027 (1), 1075 (2), 1112 (2), 1128 (3), 1244 (1), 1300 (10), 1390 (2), 1430 (10), 1440 (9), 1450 (9), 2850 (6), 2890 (4), 2934 (3), 2985 (5).

When 3-heptyl-5,5-dimethylpyrazoline is distilled in the absence of KOH and Pt a 69.3% yield of 1,1-dimethylheptylcyclopropane is obtained; it has the same constants as the hydrocarbon obtained by the catalytic decomposition of 3-heptyl-5,5-dimethylpyrazoline.

The preparation of 3,5,5-trimethylpyrazoline. 3,5,5-Trimethylpyrazoline was obtained from mesityl oxide and hydrazine hydrate.

B. p. 157-159°, d_4^{20} 0.9002, $n^{20}D$ 1.4570, MR_D 33.50; calc. 33.80. Literature data: b. p. 160.5° (764 mm), d_4^{20} 0.8997, $n^{20}D$ 1.4566 [2].

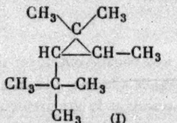
The thermal decomposition of 3,5,5-trimethylpyrazoline. The decomposition was carried out in a catalytic horizontal oven filled with glass wool (25-50 cc). The pyrazoline base was fed to the oven from an automatic buret with a volumetric rate of 0.4. The liquid decomposition product was collected in a receiver cooled with ice and salt; the waste gas was collected in a gas holder. It was established that the base only begins to decompose at 340°, which is observable by the liberation of gas; intense decomposition takes place at 420-440°. 44 ml of base was passed through in 5 hrs; 41 ml was recovered. 1.5 ml of condensate was obtained from two experiments. 2.5 liters of gas was obtained. The condensate (1 ml) which was evidently a mixture of 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene was washed with 50% CH_3COOH, a 25% NaOH solution and water, dried with $CaCl_2$ and distilled.

B. p. 56-70°, d_4^{20} 0.7057, $n^{20}D$ 1.4060, MR_D 29.27; calc. 29.44. Literature data: 2,3-dimethyl-1-butene, b. p. 58°; 2,3-dimethyl-2-butene, b. p. 71-73° [16].

When the 56-70° fraction was brominated crystals of tetramethylethylene dibromide were obtained.

Analysis of the gas (in %): unsaturated hydrocarbons 1.9, ethylene 0.00, hydrogen 0.54, methane 71.50, nitrogen 26.06.

In conclusion, a number of observations may be made regarding the combined dispersion spectra which confirm the cyclic structure of the above-described hydrocarbons (I)-(III).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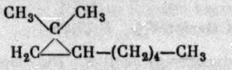
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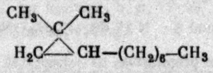
(III)

Lines in the 3000 cm^{-1} region, characteristic of CH and CH_2 groups in a three-membered ring, are contained in these spectra. In addition, in the spectra of hydrocarbons (II) and (III) two frequencies (1112 and 1130 cm^{-1}) are observed which are found in the spectrum of 1,1,2-trimethylcyclopropane and probably belong to the frequencies of a ring somewhat reduced (in comparison with 1200 cm^{-1}) as a result of the presence of substituents. Only the frequency 1109 cm^{-1} was definitely found in the spectrum of hydrocarbon (I). In the spectra of hydrocarbons (II) and (III) the frequency 1305 cm^{-1} which belongs to the CH_2 group of an aliphatic chain is also found. As in the spectrum of 1,1,2-trimethylcyclopropane, intense lines in the 680-700 cm^{-1} region, due to the presence of a gem-substituted carbon atom, are found in the spectra of these hydrocarbons.

The authors wish to express their thanks to V. P. Kuznetsov who took part in the investigation of the combined dispersion spectra.

SUMMARY

1. The pyrazoline bases 3-N-pentyl-5,5-dimethyl- and 3-N-heptyl-5,5-dimethylpyrazolines, which when distilled at atmospheric pressure decompose with the liberation of nitrogen and cyclopropane hydrocarbons, were obtained for the first time from β-chloroketones. It was established that bases containing alkyl groups of normal structure in the molecule decompose far more readily than bases having branched alkyl groups.

2. 1,1-Dimethyl-2-N-pentylcyclopropane, 1,1-dimethyl-2-N-heptylcyclopropane and a mixture of 1,3-dimethyl-3-neopentylcyclopropane and 1,2,2-trimethyl-3-tert -butylcyclopropane were obtained for the first time.

3. The combined dispersion spectra of gem-substituted cyclopropane hydrocarbons were obtained and their characteristic frequencies were indicated.

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THE INVESTIGATION OF TRITERPENES

II. THE STRUCTURE OF ZEORIN

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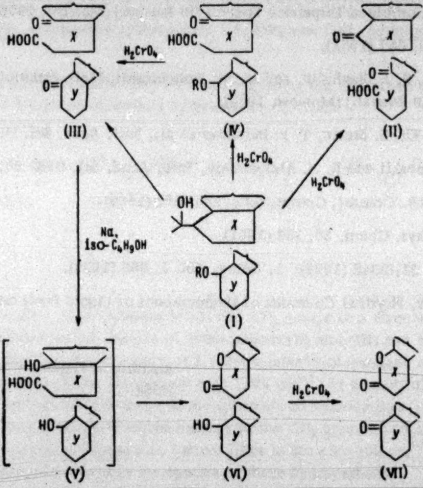
We established [1] that the triterpene alcohol zeorin with the composition $C_{30}H_{52}O_2$ (I, R = H) has an isopropyl group adjoining the X ring and combined with a tertiary hydroxyl group. The other hydroxyl group, which has a secondary character, is located in one of the six-membered Y rings [2]. When zeorin is oxidized with chromic acid, acetone and a diketo acid $C_{27}H_{42}O_4$ are formed; this can be reprepresented by one of two systems: (I, R = H)→ (II) or (I, R = H) → (III).



If the reaction takes place according to the latter system the oxidation of zeorin monoacetate (I, R = CH_3CO) should lead to the formation of an acetoxyketo acid (IV, R = CH_3CO) which after saponfication and further oxidation with chromic acid would be converted to a diketo acid (III). The experiment we carried out gave precisely these results. The carboxy and, therefore, the second ketone group of the diketo acid are, in consequence, formed by the decomposition of the X ring.

When the diketo acid (III) is reduced with sodium in isobutyl alcohol the dihydroxy acid (V) is formed which is converted to the oxylactone (VI), even during the process of formation. This oxylactone is readily oxidized by chromic acid to the ketolactone (VII). Both lactones are slowly saponified by the titration of their solutions in dioxane with caustic potash at 100°. The potassium salt obtained from the ketolactone was converted to the crystalline silver salt. The hydroxyketo acid (IV, R = H) does not form a lactone even when acted on by a solution of sulfuric acid. It must, therefore, be assumed that the hydroxyl located at the point of rupture of the ring X takes part in the formation of the lactone ring. Zeorin, which is a saturated pentacyclic triterpene $C_{30}H_{52}O_2$ and has a side chain of three carbon atoms, must be formed of four six-membered and one five-membered ring. Comparing this fact with the readiness with which the dihydroxy acid (V) forms a lactone we may assume that the X ring in the zeorin molecule must be a five-membered one, while the ring in the lactone molecule must be six-membered. The isopropyl group must be connected to the X ring in the α-position with respect to the connecting point of the rings, which is the usual structure in triterpene compounds of the lupane group.

The structure of the diketo acid and the lactones was confirmed by a spectroscopic investigation. Two absorption maxima, at 1700 and 1725 cm^{-1}, were discovered in the infrared spectrum of the methyl ester of the diketo acid (III). The first maximum corresponds to the keto group in the six-membered ring, the second maximum corresponds to the carbonyl of the ester group. The spectrum of the hydroxylacetone (VI) in the region of the carbonyl groups has only one absorption maximum corresponding to the carbonyl group in the six-membered ring of the lactone. In addition, it has a maximum at 3475 cm^{-1}, absent in the spectrum of the two other substances; this indicates the development of a hydroxyl group which takes part in the formation of an intramolecular hydrogen bond. Two maxima (at 1694 and 1743 cm^{-1}), associated with the keto group and the carbonyl group of the lactone ring, respectively,* are again found in the ketolactone (VII). The character of the keto groups agrees with the structure we assumed for the investigated compounds. The keto group located in the ring Y is inactive in zeorinone and does not condense with semicarbazide [2]; the diketo acid forms a monosemicarbazone [1] and the ketolactone does not give a condensation product with semicarbazide.

Investigating the crystalline ozonide, previously obtained [1], we established that as a result of catalytic hydrogenation it is converted to the diketone $C_{32}H_{52}O_4$. This determines the tertiary-tertiary character of the double bond of zeorinine.

By dehydrating zeorin in acetic acid solution in the presence of 5% sulfuric acid we obtained two diene hydrocarbons; it was not possible to identify these substances with known compounds.

EXPERIMENTAL

1. Oxidation of zeorin monoacetate (I, R = CH_3CO). 8.54 g of zeorin monoacetate in 150 ml of acetic acid was oxidized at 42-44° with chromic acid obtained from 7.2 g of chromic anhydride. The solution was diluted with water, acidified with hydrochloric acid and the reaction products were extracted with ether. The ethereal solution was washed with water, the acid (IV, R = CH_3CO) was extracted with a solution of potash, precipitated with hydrochloric acid and saponified by boiling in a 25% methanol solution of caustic potash. As a result, 4.0 g of an indistinctly crystalline hydroxyketo acid (IV, R = H) was obtained. 1 g of this acid was oxidized in an acetic acid solution of 1 equiv. of chromic acid and the diketo acid (III) which melted at 244.5-245.5° (corr.) after recrystallization was obtained; the melting point of the methyl ester was 145.5-146.5° (corr.). The substances were identified by mixed melts with the corresponding compounds obtained previously [1]. The hydroxyketo acid (IV, R = H) did not form a lactone when its solution was heated in acetic acid containing 3% sulfuric acid for 40 min at 80°.

2. Hydroxylactone (VI). A solution of 8.95 g of diketo acid in boiling isobutyl alcohol was treated with sodium. The reaction mixture was washed with water and shaken with sulfuric acid after which crystallization of the hydroxylactone in the alcoholic layer commenced. The yield of the product was 5.5 g. After recrystallization from dioxane the m. p. was 230-231° (corr.).

Found %: C 78.14, 78.19; H 10.78, 10.95. $C_{27}H_{44}O_3$. Calculated %: C 77.83; H 10.64.

3. The ketolactone (VII). 4 g of the hydroxylactone was suspended in 400 ml of acetic acid and was oxidized at room temperature with chromic acid prepared from 1 g of anhydride. 2.5 g of ketolactone was obtained. After recrystallization from dioxane it was in the form of needles with a m. p. of 361.5° (corr.). A mixture with the hydroxylactone melted at 305-310°.

Found %: C 77.84, 77.85; H 10.50, 10.54. $C_{27}H_{42}O_3$. Calculated %: C 78.21; H 10.21.

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* All the substances were investigated in the form of suspensions in vaseline oil.

After the solution of the ketolactone and semicarbazide hydrochloride in pyridine had been allowed to stand for several days the initial substance was obtained. In a boiling dioxane solution the lactone slowly saponifies during titration with caustic potash. When a solution of the potassium salt obtained was mixed with an aqueous dioxane solution of silver nitrate the crystalline silver salt was precipitated.

Found %: Ag 20.16, 20.13. $C_{27}H_{43}O_4Ag$. Calculated %: Ag 19.63.

4. Acetoxydiketone. 3.20 g of the ozonide of acetylzeorine was hydrogenated in an ethereal solution with palladinized barium sulfate. 3.02 g of a crystalline substance was obtained. After several recrystallizations from alcohol it melted at 123-124° (corr.).

Found %: C 76.98, 76.80; H 10.65, 10.61. $C_{32}H_{52}O_4$. Calculated %: C 76.75; H 10.47.

The diketone is not oxidized when acted on by chromic acid in acetic acid solution at room temperature for several hours. It forms a disemicarbazone with a m. p. of 220° (corr.).

Found %: N 13.67, 13.72. $C_{34}H_{58}O_4N_6$. Calculated %: N 13.67.

5. Diene hydrocarbons. 14.7 g of zeorin was heated at 100° in 300 ml of acetic acid, containing 5 ml of sulfuric acid, for 50 min. After the mixture had cooled, 7.7 g of a felt-like mass of fine needles was filtered. After recrystallization from acetone or acetic acid the substance melted at 181-182° (corr.), $[\alpha]_D$ 47.6° (c 4.22).

Found %: C 87.95, 87.92; H 12.24, 12.26. $C_{30}H_{48}$. Calculated %: C 88.16; H 11.84.

The tarry mass which precipitated out when the acetic acid mother liquor was diluted with water was chromatographed from petroleum ether on aluminum oxide; a hydrocarbon with a m. p. of 137-143° was obtained. The substance remained unchanged with repeated chromatography and recrystallization.

Found %: C 87.87, 87.85; H 11.77, 11.76. $C_{30}H_{48}$. Calculated %: C 88.16; H 11.84.

It should be noted that the analysis of some of the compounds obtained from zeorin by various authors, including those we obtained in this work, leads to the formula $C_{30}H_{50}O_2$ for zeorin. The analysis of the great majority of compounds, however, agrees with the formula $C_{30}H_{52}O_2$. We carried out numerous analyses of zeorin, purified by various methods, and confirmed the latter formula. In giving the results of the analyses of the substances investigated by us, we therefore compare them with the theoretical results on the basis of this formula.

SUMMARY

1. It was established that the triterpene alcohol zeorin has a five-membered ring to which an isopropyl group is joined in the α-position with respect to the connecting point of the ring and the neighboring ring. This structure is found in derivatives of lupane. The formation of the previously-described diketo acid takes place by the rupture of this five-membered ring.

2. By splitting the ozonide of acetylzeorinine a ketone was obtained, indicating the tertiary-tertiary character of the double bond of zeorinine.

3. By dehydrating zeorin, two diene hydrocarbons distinct from the initial substances were obtained.

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* Original Russian pagination. See C. B. translation.

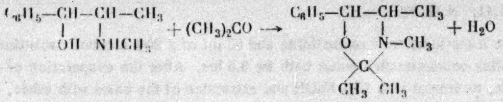
THE CONDENSATION PRODUCTS OF L-EPHEDRINE AND D-PSEUDOEPHEDRINE WITH ACETONE

L. G. Matsova and A. S. Labenskii

As is known, aminoethanols react with aldehydes and ketones forming condensation products which are derivatives of oxazolidines [1]. In the case of ephedrine and pseudoephedrine only condensation products of these alkaloids with benzaldehyde are known [2].

Working with D-pseudoephedrine we found that the mother liquor obtained in the recrystallization of D-pseudoephedrine from acetone contains an unknown substance. We isolated the latter and characterized it. The compound obtained was a colorless oily product which readily distills under vacuum. The salts of this substance were also prepared and characterized. We then obtained the same substance by boiling D-ephedrine with acetone. It was found that the presence of alkaline activated charcoal appreciably accelerates the reaction.

On the basis of the method of preparation of the substance and also from the established elementary composition and the determination of the molecular weight of the hydrochloride of the substance it may be assumed that the substance is an oxazolidine derivative formed by the condensation of D-pseudoephedrine with acetone.



$$C_6H_5\text{—}CH(OH)\text{—}CH(NHCH_3)\text{—}CH_3 + (CH_3)_2CO \longrightarrow C_6H_5\text{—}\underset{O}{CH}\text{—}\underset{N\text{—}CH_3}{CH}\text{—}CH_3\ \left[>C(CH_3)_2\right] + H_2O$$

All the data we obtained confirmed this assumption. For instance, as a result of the acid hydrolysis of the compound obtained, D-pseudoephedrine was isolated. This fact agrees with previous information [1, 3], according to which, as a result of similar hydrolysis, oxazolidine derivatives readily split up with the formation of the corresponding aminoethanols.

The investigation of the infrared spectrum of the substance showed the absence of an absorption maximum in the 3520-3110 cm^{-1} region, characteristic of a hydroxyl group, and also in the 3500-3100 cm^{-1} and 1580-1510 cm^{-1} regions, characteristic of a secondary amino group. The infrared spectrum of D-pseudoephedrine has a corresponding absorption maximum.

The determination of the value of the molecular refraction also confirmed the above-mentioned assumption regarding the structure of the substance obtained, which in accordance with the work of Hückel [4] and Close [5] can be determined as D-trans-2,2,3,4-tetramethyl-5-phenyloxazolidine.

In view of the fact that certain compounds of similar structure possess physiological activity [6], the hydrochloride of the compound we obtained was subjected to a corresponding investigation. It was found that this compound has weak adrenomimetric and spasmolytic effects compared with already-known remedies.*

By analogy with the above-mentioned reaction we condensed L-ephedrine with acetone. The mixture was boiled until a constant angle of rotation of the reaction mass was obtained. As a result of the reaction we obtained an oily substance which distilled under vacuum. The substance became crystalline on standing in a refrigerator. The ultimate analysis and also the result of acid hydrolysis which leads to the formation of L-ephedrine proves that the compound we obtained is D-cis-2,2,3,4-tetramethyl-5-phenyloxazolidine.

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* The pharmacological investigation of the substance was carried out by Iu. I. Syrneva.

We also obtained and characterized the picrate of D-cis-2,2,3,4-tetramethyl-5-phenyloxazolidine. The hydrochloride and perchlorate were also obtained. It was impossible to purify the latter substances for analytical purposes because of their instability.

It should be noted that it requires a considerably longer time (25 hrs) to complete the condensation reaction of L-ephedrine and acetone than for the analogous reaction with D-pseudoephedrine (5 hrs). This difference can be explained by the different spatial structure of these compounds as a result of which the condensation of ephedrine encounters steric hindrance [7].

EXPERIMENTAL

1. 20 g of D-pseudoephedrine with 70 ml of acetone and 0.5 g of alkaline activated charcoal were boiled with a reflux condenser on a water bath for 5 hrs. After the solution had been filtered from the charcoal the filtrate was evaporated. The oil remaining was distilled under vacuum. The yield was 22.4 g (90%).

B. p. 117° at 8 mm, $[\alpha]_D$ +34.92°, d_4^{20} 0.9823, $n^{18.5}D$ 1.5085, MR_D 62.19; calc. 62.016. Found %: C 75.83; H 9.20; N 7.07. $C_{13}H_{19}ON$. Calculated %: C 76.06; H 9.33; N 6.82.

The hydrochloride was obtained by mixing ethereal solutions of the base and hydrogen chloride.

After it had been recrystallized twice from a mixture of acetone and methanol, the m. p. was 181-182°, $[\alpha]_D$ +46.9° (c 9.2; water). Found %: C 64.67; H 8.51; N 5.77; Cl 14.50. M (by Rast's method) 233; M (by titration) 240.2. $C_{13}H_{20}ONCl$. Calculated %: C 64.71; H 8.28; N 5.80; Cl 14.67. M 241.76.

The picrate was obtained by mixing alcoholic solutions of the base and picric acid.

After the picrate had been recrystallized from a mixture of acetone and methanol, the m. p. was 142-143° (decomp.). $[\alpha]_D$ −41.3 (c 4.6; acetone). Found %: C 52.69; H 5.22; N 13.14. $C_{13}H_{19}ON \cdot C_6H_3O_7N_3$. Calculated %: C 52.70; H 5.11; N 12.90.

2. 5.52 g of the trans-substituted oxazolidine and 50 ml of a 20% alcoholic solution of hydrogen chloride were boiled with a reflux condenser on a water bath for 3.5 hrs. After the evaporation of solution, the addition of water to the residue, treatment with 10% NaOH and extraction of the bases with ether, a mixture of oil and crystals was obtained. The latter were filtered, washed with a small amount of acetone and then dried. The yield was 1.2 g. The crystals were identified by direct comparison with D-pseudoephedrine.

3. 16.15 g of L-ephedrine was boiled with 70 ml of acetone and 0.5 g of alkaline activated charcoal for 25 hrs with a reflux condenser on a water bath. After the charcoal had been removed the filtrate was evaporated. The oil which remained was distilled under vacuum. The yield was 17.0 g (85%).

B. p. 116° at 7.5 mm, m. p. 26-34° (in a sealed capillary), $[\alpha]_D$ +19.1° (c 7; acetone). Found %: C 75.73; H 9.32; N 6.95. M (by titration) 206.5. $C_{13}H_{19}ON$. Calculated %: C 76.06; H 9.33; N 6.82. M 205.36.

The picrate was obtained by adding an alcoholic solution of picric acid to the hot alcoholic solution of the base.

M. p. 180.5-182°, $[\alpha]_D$ −64.3° (c 0.4; acetone). Found %: C 52.45; H 5.13; N 12.79. $C_{13}H_{19}ON \cdot C_6H_3O_7N_3$. Calculated %: C 52.70; H 5.11; N 12.90.

The perchlorate was obtained by adding hydrochloric acid to an alcoholic solution of the base. The m. p. was 183-184°, $[\alpha]_D$ −17.75° (c 1; acetone). After recrystallization from anhydrous alcohol the m. p. was 174-176°; when heated under vacuum the substance turned pink.

The hydrochloride was obtained by mixing an ethereal solution of the base and an alcoholic solution of hydrogen chloride. The m. p. was 151-164°. After recrystallization from acetone-methanol mixture the m. p. was 153-164°, $[\alpha]_D$ −38.24° (c 1.4; water). A crystalline product was obtained from the mother liquor.

4. A solution of 1 g of cis-substituted oxazolidine in 10 ml of alcohol was boiled with 10 ml of 17% alcoholic hydrochloric acid with a reflux condenser on a water bath for 3.5 hrs. A crystalline precipitate was obtained when the solution was cooled. The weight was 0.42 g. The identity of the precipitate was established by a mixed melt with L-ephedrine hydrochloride (no depression) and by the value of the specific rotation.

SUMMARY

The condensation products of L-ephedrine and D-pseudoephedrine with acetone and their salts were obtained for the first time.

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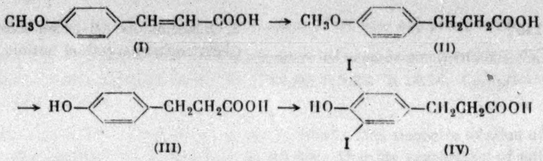
HORMONES OF THE THYROID GLAND AND THEIR ANALOGS

IV. THE SYNTHESIS OF DESAMINO ANALOGS OF BETAZINE (β-DIIODOTYROSINE)

N. N. Suvorov, L. M. Morozovskaia, and A. A. Dudinskaia

In previous communications [1] we described the synthesis of a new antithyrotropic preparation "betazine" (β-diiodotyrosine) and a number of β-amino acids which are isomers and analogs of the latter. To investigate the relationship between the physiological action and the chemical structure it was of interest to study the activity of the corresponding substituted propionic acids, i. e., compounds without an amino group in the side chain.

We synthesized β-(4-hydroxy-3,5-diiodophenyl)propionic acid by the following system: p-methoxycinnamic acid (I) was hydrogenated over Raney nickel, the product (II) obtained was demethylated by boiling with hydrobromic acid and the p-hydroxycinnamic acid (III) was iodized by Lugol's solution in ammonia.



It must be pointed out that β-(4-hydroxy-3,5-diiodophenyl)propionic acid has been described in literature and was obtained by the iodination of p-hydroxyhydrocinnamic acid (III) with iodine in a solution of caustic soda [2].

The method we proposed for obtaining p-hydroxyhydrocinnamic acid is original.

We also obtained 3-hydroxy- and 3-aminohydrocinnamic acids by the hydrogenation of 3-hydroxy- and 3-nitrocinnamic acids, respectively, over Raney nickel. Their iodination was carried out according to literature data [3, 4].

The physiological activity of the compounds obtained will be reported elsewhere.

EXPERIMENTAL

p-Methoxyhydrocinnamic acid (II). 15.5 g of p-methoxycinnamic acid (I) was hydrogenated in 77 ml of ethyl alcohol over Raney nickel (~ 3 g) at 30 atmos and 80°. The solvent was distilled off under vacuum, the residue was crystallized from a mixture of 45 ml of alcohol and 60 ml of water, employing activated charcoal to decolorize the solution. 13.8 g of a product with a m. p. of 102-103° was obtained. It was possible to obtain a further 0.5 g of fairly pure acid from the mother liquors. The total yield was 91%. Literature data: m. p. from 101-104° [5].

p-Hydroxyhydrocinnamic acid (III). 7 g of p-methoxycinnamic acid (II) was boiled with stirring with 35 ml of 40-48% hydrobromic acid until the oil which was initially formed had completely dissolved (about 4 hrs). The solution was then cooled and the precipitated p-hydroxyhydrocinnamic acid was filtered through a glass filter.

It was crystallized from 7 ml of 10% aqueous alcohol with activated charcoal. The yield was 5.56 g (86%). The m. p. was 126.5-129°. Literature data: m. p. from 128-130° [5].

β-(4-Hydroxy-3,5-diiodophenyl) propionic acid (IV). A solution of 6.7 g of iodine and 5.7 g of potassium iodide in 26 ml of water was added to a solution of 2 g of p-hydroxyhydrocinnamic acid in 14 ml of 12% aqueous ammonia at 5° over a period of 30 min. After 1 hr the excess iodine was removed by adding sodium bisulfite and the iodine-containing acid was precipitated with hydrochloric acid. After 3 crystallizations from aqueous alcohol 2.02 g (40%) of a substance with a m. p. of 161-162° was obtained (Bougault [2] indicates a m. p. of 162°).

Found %: I 60.57. $C_9H_8O_3I_2$. Calculated %: I 60.70.

β-(3-Hydroxy-2,4,6-triiodophenyl) propionic acid. A mixture of 12.4 g of m-hydroxybenzaldehyde, 18.5 g of malonic acid, 19 ml of pyridine and several drops of piperidine was boiled for 4.5 hrs and when cool it was poured into 105 ml of hydrochloric acid (1 : 2). The precipitate deposited was filtered, washed with water and dried. 14.8 g (89%) of m-hydroxycinnamic acid with a m. p. of 191-192° (from aqueous methanol) was obtained.

9.58 g of this acid was hydrogenated over Raney nickel in 96 ml of ethyl alcohol at 30 atmos and 80°. 7.45 g (77%) of m-hydroxyhydrocinnamic acid was obtained. The latter was iodized with iodine monochloride in glacial acetic acid. The m. p. was 225-226° (from a 1 :1 mixture of acetone and water). Literature data: m. p. 225-226° [3].

β-(3-amino-2,4,6-triiodophenyl) propionic acid was obtained in similar manner from m-nitrobenzaldehyde.

SUMMARY

1. Desamino analogs of betazine were prepared for pharmacological purposes: β-(4-hydroxy-3,5-diiodo)-, β-(3-hydroxy-2,4,6-triiodo)- and β-(3-amino-2,4,6-triiodo) phenylpropionic acids.

2. A new convenient method of preparing p-hydroxyhydrocinnamic acid was proposed.

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THE SPECTROPHOTOMETRIC INVESTIGATION OF THE REACTION OF CHLOROPHYLL WITH FERRIC CHLORIDE

S. S. Butsko and B. Ia. Dain

It is known that considerable amounts of iron salts are contained in the chlorophyll-bearing plastids of the green leaves of plant organisms [1]. Certain data indicate the presence of a close bond between these salts and chlorophyll and its protein carrier [2]. In this connection the problem of the nature of the chemical reactions which can take place in corresponding associates is of interest.

It is natural to expect that under favorable circumstances the iron ions must displace magnesium from the chlorophyll nucleus with the formation of a hemin structure. The data of Barnes and Dorough [3], who observed a number of reactions of the displacement of one metal by another in metallotetraphenylporphins, are particularly in favor of such an assumption. The investigation of processes of this type in chlorophyll is of particular importance in connection with the interesting optical properties of hemin-like analogs of chlorophyll, making probable their participation in the photochemical phase of photosynthesis [4]. On the other hand, Rabinowitch and Weiss [5] gave a number of data which suggested that in alcoholic solution trivalent iron ions reversibly oxidize chlorophyll in darkness with the formation of a hypothetical oxidized form according to the system.

$$Fe^{+++} + Chl \rightleftarrows Fe^{++} + oxyChl^{*}. \qquad (1)$$

The presence of such a reaction would signify that even in the dark an unstable product with a high oxidation potential is formed in the leaf, this product also being capable of acting as an important factor for initiating the development of the oxidation branch of the photosynthesis reaction.

The fact that the reaction of chlorophyll with ferric chloride in alcoholic solutions is complicated by side reactions which complicate the explanation of the nature of the main reaction [6] should, however, be taken into consideration. The pheophytinization of chlorophyll, which is observed in alcoholic solutions, is due to the hydrogen ions formed during the solvolysis of iron salts, and complicates the investigation markedly. As a result of this, the reversible reaction postulated by Rabinowitch and Weiss on the basis of spectral data obtained for alcoholic solutions cannot be considered as proven.

The present article gives the results of the spectrophotometric investigation of the reaction of chlorophyll with anhydrous ferric chloride in diethyl ether and acetone, solvents in which the effect of the pheophytinization of chlorophyll is practically excluded.

EXPERIMENTAL

The reaction vessel. Preliminary experiments indicated that in air (to be more precise, in the presence of dissolved oxygen) the reaction between ferric chloride and chlorophyll is complicated by side reactions. The investigation of the reactions which interested us was, therefore, carried out under high vacuum.

The investigated reaction and also the preceding operations to remove traces of air from the solutions and mix them were carried out in a seamless glass vessel connected to a high-vacuum installation (Fig. 1). Apart

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* Oxychl = oxychlorophyll.

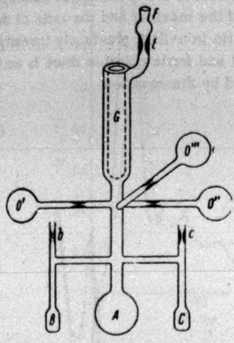

Fig. 1. Reaction vessel. Explanation in text.

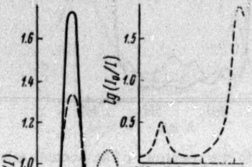

Fig. 2. Changes in the spectrum of an ethereal solution of chlorophyll a during its reaction with $FeCl_3$. Absorption curves: 1) of the initial solution; 2) after 18 hrs; 3) after 6 days. In the upper part – the absorption curve of an alcoholic solution of the reaction product of chlorophyll and $FeCl_3$.

from the main receptacle A in which the chlorophyll solution was placed, the vessel had branch pieces B and C for the ferric chloride and other reagents and also cuvettes O', O'' and O''' for spectrophotometric measurements. The cuvettes, filled under vacuum, were sealed off from the vessel and the solutions contained in it were subjected to photometry in an SF-4 spectrophotometer.

Preparations. Chlorophyll a was obtained from dry nettle leaves according to method [7] and was separated from components b by chromatography in a column with anhydrous sugar powder. The purity of the pigment was checked in each instance by the analysis of its absorption spectrum. The solvents were purified by methods given in the book [8] and were distilled again before the experiment. Anhydrous ferric and ferrous chloride which were obtained by usual methods and kept under vacuum in sealed ampules were used in the experiments.

Experimental procedure. 15 ml of a solution of chlorophyll with a concentration of $\sim 10^{-5}$ mole was introduced into the receptacle A and 1 ml of solvent and several small crystals of anhydrous $FeCl_3$ were added to the branch piece B. The branch piece was then sealed off at the constriction b. The vessel was connected to the high-vacuum installation by means of the ground-in joint F. Liquid air was poured into the trap G to prevent the vapors of the solvent from entering the vacuum system. After the solutions had been completely degassed and a high vacuum had been established, the vessel was sealed at the constriction E. Because the solvent from the lateral branch piece passed into the receptacle during the process of evacuation of the system toward the end of pumping, the ferric chloride was present in the form of a solid film on the walls of the container B. After part of the solution had been led off to the cuvette for spectrophotometric measurements and it had been sealed off from the system, the lateral branch piece was immersed in liquid air for several minutes, as a result of which, part of the solvent distilled from it into the receptacle A. The solution of ferric chloride obtained after defreezing was poured into the receptacle and was carefully shaken. The cuvettes were filled with the solution obtained, then they were sealed off from the vessel and subjected to photometry at specific periods. When it was necessary to know the exact concentrations of the solutions of salts added, appropriate, previously-prepared solutions were introduced instead of crystals in the branch piece B. The volume of liquid in the receptacle after mixing was always made up to the same level. The addition of the other reagents ($FeCl_2$, $CaCl_2$, NaCl) was carried out by a similar method via the branch piece C.

The reaction of chlorophyll with ferric chloride in a solution of ether takes place extremely slowly. The first changes in the spectrum, consisting in a certain reduction in the intensity of the red absorption band of chlorophyll at 662 mμ and the appearance of a band of the reaction product at 630 mμ, initially of low intensity, is only noted several hours after the mixing of the solutions (Fig. 2).

The intensity of this band increases slowly with simultaneous weakening of the absorption bands of chlorophyll. The latter disappear completely only after 6-7 days. After the reaction had been completed the products were brought into solution in chloroform. The separated chloroform layer was repreatedly washed with water until iron salts had been completely removed and it was then evaporated to dryness. After being carefully dried under vacuum the dry residue was dissolved in alcohol. The spectrum of the alcoholic solution of the product (shown in the upper part of Fig. 2) has two intense bands at 630 and 385 mμ and, in contrast to the spectrum of chlorophyll, does not contain vibrational bands of low intensity. As regards the position of the maxima and the ratio of their intensities, this spectrum coincides completely with the spectrum of pheophytin iron-III,* previously investigated [4]. From these data it follows that as a result of the reaction of chlorophyll and ferric chloride there is an intense displacement of magnesium by iron, which may be summarily expressed by the equation

$$\mathrm{MgPh} + \mathrm{FeCl_3} \mapsto \mathrm{FeClPh} + \mathrm{MgCl_2}. \qquad (2)$$

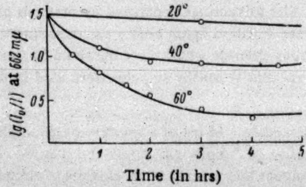

Fig. 3. The influence of temperature on the rate of introduction of iron into the nucleus of chlorophyll.

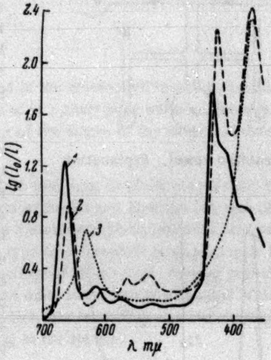

Fig. 4. Changes in the spectrum of an acetone solution of chlorophyll a during its reaction with $FeCl_3$. Absorption curves: 1) of the initial solution of chlorophyll a, 2) directly after the introduction of $FeCl_3$, 3) after 5 days.

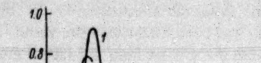

Fig. 5. The influence of oxygen on the process of the introduction of iron into the chlorophyll nucleus. Absorption curves: 1) of the gray intermediate product, 2) after the admission of air, 3) after keeping in air for 10 days.

This was confirmed by additional experiments in which the reaction product was isolated in the pure form and ashed. Iron and chlorine were found in the ash of the product and the absence of magnesium was established. The exposure of an alcoholic solution of the product to light leads to its reduction (the appearance of bands at 655 and 410 mμ and the disappearance of the bands at 630 and 385 mμ), which is characteristic for pheophytin iron-III [4].

The slow course of the reaction is evidently associated with the high energy of activation. In fact, an increase in temperature markedly accelerates the reaction, as follows from a comparison of the velocity curves for 20, 40 and 60° given in Fig. 3.

The course of the reaction in acetone solution shows interesting features which are essential for understanding its mechanism. In this instance also, the end product is pheophytin iron-III. In this solvent, however, fundamental spectral charges are detected immediately after the introduction of the iron salt (Fig. 4). The green solu-

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* Pheophytin iron, the product of the substitution of the central atom of magnesium in the chlorophyll nucleus by iron, exists in oxidized (FeX complexes where X is hydroxyl or an acid residue) and reduced forms (Fe complex). The oxidized form of this derivative of chlorophyll and its analogs was investigated in [9, 10]. The reduced product was obtained by the photochemical reduction of the oxidized form [4]. The abbreviations MgPh, FeClPh, FePh, where Ph is the organic nucleus of chlorophyll without metal, will be used subsequently for chlorophyll and these derivatives, respectively.

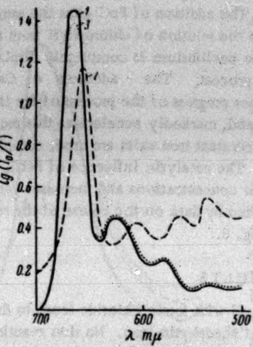

Fig. 6. The influence of additions of CaCl$_2$. Absorption curves: 1) of the initial solution of chlorophyll a in acetone; 2) after the introduction of FeCl$_3$; 3) after the addition of CaCl$_2$.

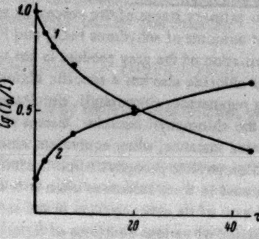

Fig. 7. The influence of additions of CaCl$_2$ on the intensity of the absorption maxima of regenerated chlorophyll and pheophytin iron. 1) Absorption of regenerated chlorophyll at 662 mμ; 2) Abs. of the product formed in the reaction, 630 mμ; τ) time (in hrs), elapsed from the moment of the formation of gray product until the introduction of CaCl$_2$.

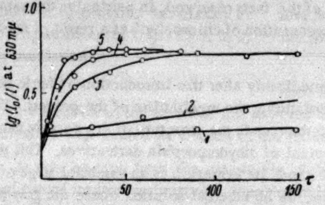

Fig. 8. The influence of additions of FeCl$_2$ on the rate of introduction of iron into the chlorophyll nucleus. Curves of the variation of $\log(I_0/I)$ for $\lambda = 630$ mμ with respect to time (in min): 1) without additions of FeCl$_2$. Conc. of FeCl$_2$ (in mole/liter): 2) $6 \cdot 10^{-6}$, 3) $1.8 \cdot 10^{-5}$, 4) $2.4 \cdot 10^{-5}$, 5) $3 \cdot 10^{-5}$.

tion becomes grayish. The red absorption band of chlorophyll (662 mμ) is considerably reduced and is somewhat displaced toward the shortwave side, up to 655 mμ. Other bands appear simultaneously: bands of low intensity at 605, 565, and 535 mμ and two very intense bands at 420 and 370 mμ. The spectrum of the gray product is fairly stable and is accurately reproduced in all the experiments. On long standing the intensity of its characteristic absorption bands is gradually reduced. Bands of pheophytin iron-III appear simultaneously. The reaction proceeds somewhat more rapidly than in ethereal solutions. It is markedly retarded, however, if the solution containing the gray product is brought into contact with air. In this instance it is not possible to observe an appreciable increase in the intensity of the absorption band at 630 mμ, belonging to pheophytin iron, even after 10 days (Fig. 5); this indicates the extremely marked retarding influence of oxygen on the process of the introduction of iron into the center of the porphin nucleus.

The initial changes found in the spectrum of chlorophyll as a result of the introduction of ferric chloride are reversible. The initial state may be re-established by adding chlorides (solutions of NaCl, CaCl$_2$, etc.) (Fig. 6). Complete regeneration of chlorophyll is, however, attained only when these salts are introduced immediately after the formation of the gray product. The regeneration of the chlorophyll is otherwise found to be incomplete and a maximum at 630 mμ, belonging to pheophytin iron, appears simultaneously in the spectrum. The intensity of this maximum is greater the longer the time from the moment of formation of the gray product to the introduction of the chloride. The reverse relationship is found for the red maximum of regenerated chlorophyll (Fig. 7). A considerable degree of regeneration of chlorophyll can, nevertheless, be noted even after 20-25 hrs. This fact indicates that the gray intermediate product is not labile and has a very long life.

From the data given it follows that the investigated process in acetone solution takes place in two stages. The first of these, associated with the formation of the intermediate product, is reversible. The second, in which the end product is formed, is irreversible. The process may be represented according to the following system:

$$\mathrm{FeCl_3 + MgPh} \rightleftarrows \text{Intermediate product} \longrightarrow \mathrm{FeClPh + MgCl_2}. \qquad (3)$$

Catalysis by iron ions. As we saw above, the action of NaCl and $CaCl_2$ on the gray intermediate product displaces the primary stages of the process in system (3) to the left. The addition of $FeCl_2$ has the same action. If equivalent amounts of anhydrous $FeCl_3$ and $FeCl_2$ are introduced in the solution of chlorophyll from the very start, the formation of the gray product is not noted at all because the equilibrium is completely displaced to the left. Ferrous chloride also has a specific action on the course of the process. The addition of $CaCl_2$ and NaCl, which regenerates chlorophyll, simultaneously retards the further progress of the process of the introduction of iron into the chlorophyll nucleus; ferrous chloride, on the other hand, markedly accelerates this process. In the investigated instance, when equivalent amounts of bivalent and trivalent iron salts are used, complete conversion of chlorophyll to pheophytin iron is attained after 10-15 min. The catalytic influence of $FeCl_2$ is already clearly indicated in those instances when it is added in negligibly low concentrations and increases very markedly with the increase of its concentration in the solution. This is illustrated by data on the course of the reaction during the period of various additions of ferrous chloride, given in Fig. 8.

DISCUSSION OF RESULTS

From the data obtained it follows that the reaction of chlorophyll with ferric chloride leads to the displacement of magnesium from the chlorophyll by iron and the formation of pheophytin iron. No side reactions occur in this process. The hypothesis of the reversible oxidation of chlorophyll to its oxy form, advanced in previous investigations [5], is therefore not confirmed. In the interpretation of the mechanism of the reaction we take as our basis the assumption that it is effected between molecules of chlorophyll and molecules of ferric chloride or its ions. The latter is assumed for acetone solutions in which the ionic dissociation is fairly strongly expressed. A purely ionic interpretation of the exchange reaction observed must obviously be rejected. It is hardly possible to admit an appreciable dissociation of the chlorophyll molecules in a nonaqueous solvent. At the same time if such an admission is made it is impossible to explain a number of the facts observed, in particular the catalysis of the process by bivalent iron ions and also the effect of the regeneration of chlorophyll as a result of the addition of chlorides.

The problem of the nature of the gray product formed immediately after the introduction of ferric chloride in a solution of chlorophyll in acetone is very essential for understanding the mechanism of the process. The formation of this product is not associated with any significant disturbances in the structure of the porphin nucleus of chlorophyll, this being indicated by the spectrum which is typical of dihydroporphin derivatives. This product is very stable, which is confirmed by its long life. On the other hand, its formation is an essential stage of the reaction, ensuring the necessary conditions for its further progress. In an ethereal solution where the gray product is not formed the reaction takes place extremely slowly. In acetone, however, particularly in the presence of Fe^{++} ions, it can take place very rapidly. This justifies the consideration of the gray product as the active intermediate reaction product.

The primary changes observed in the spectrum of chlorophyll as a result of the introduction of ferric chloride are the result of the formation of $Fe(MgPh)^{+++}$ ions for which the conditions are favorable in acetone solutions. These particular complex ions are carriers of those properties which were noted in the gray product. In fact, as a result of the formation of such complexes the iron ion inevitably established a bond with the quaternary nitrogen atoms of the chlorophyll nucleus. This must lead to the labilization of the bonds of these atoms with magnesium which also creates favorable conditions for its displacement from the molecule. It is precisely this which determines the role of the gray product in the development of the reaction. The polarization effects which must take plase as a result of the reaction of the $Fe(MgPh)^{+++}$ ions with the chlorine ions must lead to the decomposition of these complexes and the regneration of chlorophyll. This explains the influence of chlorides in the first stage of the process which was observed in our work.

The labilization of the bonds between magnesium and the central nitrogen atoms of the chlorophyll nucleus which is evidently attained in the complex $Fe(MgPh)^{+++}$ ions is a necessary but insufficient condition for the realization of the reaction. This is indicated by its fairly slow progress in the absence of Fe^{++} ions. Here it is possible that certain steric factors also play a part because the chlorine atom must be attracted into the porphin nucleus as well as trivalent iron. The catalytic influence of Fe^{++} ions is evidently associated with the fact that they first enter the labilized nucleus of chlorophyll, which is represented by the equation (4a)

$$Fe(MgPh)^{+++} + Fe^{++} \rightarrow FePh + Mg^{++} + Fe^{+++} \qquad (4a)$$

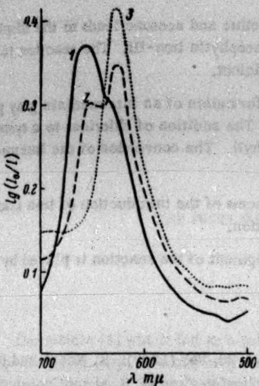

Fig. 9. The absorption curves for the product of the introduction of Fe into the chlorophyll nucleus showing the influence of the photoreduction of the original $FeCl_2$ solution. Irradiation of the $FeCl_2$ solution (in hrs): 1) 5, 2) 2, 3) no irradiation.

The formation of the end product takes place as a result of the oxidation of reduced pheophytin iron by iron chloride

$$FeCl_3 + FePh \longrightarrow FeClPh + FeCl_2 \qquad (4b)$$

a reaction which as indicated by separate experiments, takes place extremely slowly.*

The particular feature of the proposed reaction system** consists in the fact that it leads to a chain mechanism in connection with the regeneration of ferrous chloride in stage (4b). Even very low concentrations of Fe^{++} ions, therefore, cause a considerable displacement effect of magnesium by iron from the chlorophyll nucleus. From all the data the intense retardation of the reactions by oxygen which was observed in our work is associated with the rupture of the reaction chains which takes place as a result of the oxidation of the Fe^{++} ions.*** To obtain a final confirmation of the reaction system it is extremely important to realize the individual stage (4a). This is complicated, however, by the fact that in the presence of ferric chloride the second stage (4b) also proceeds immediately. In the absence of it, however, the required conditions for the reaction (4a) to take place are not present. In the supplementary experiments described below conditions under which only traces of ferric chloride were present in the reaction mixture of chlorophyll and ferrous chloride were ensured; it was therefore possible to detect the product of the first stage of the reaction.

Ferrous chloride which had been kept for some time in air was used for the experiments. In two of the three experiments carried out (Fig. 9) a solution of the salt was first exposed to irradiation by a mercury quartz lamp in order to partially reduce the trivalent iron formed as a result of the oxidation of the Fe^{++} ions.

As may be seen from the data in Fig. 9, in both experiments the reaction with chlorophyll led to the formation of two of its iron derivatives: pheophytin iron-II (absorption maximum at 655 mμ[4]) and pheophytin iron-III (absorption maximum at 630 mμ). Since the content of Fe^{+++} ions (and, therefore, $Fe(MgPh)^{+++}$ ions also) was extremely small, the introduction of iron was an extremely slow process in both experiments. The end state of the system in the experiment with a high content of trivalent iron was attained far more rapidly (in 6 hrs), however, whereas when the period of irradiation was less, the reaction took a day.

In the third experiment, in which the solution of $FeCl_2$ was not irradiated the reaction took place in 40 min and led to the formation of a single product, pheophytin iron-III.

We feel that these experiments give a convincing and very graphic proof of the reality of the above-proposed reaction system. This system is also applicable for those instances when the reaction proceeds without special additions of ferrous chloride. The traces of this salt which are unavoidably present in solution of ferric chloride in an organic solvent should be sufficient for the realization of the reaction according to the above-described catalytic mechanism.

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* The oxidation-reduction potential of the system $Fe^{III}Ph/Fe^{II}Ph$, like other analogous hemin systems, is far less positive than the system Fe^{III}/Fe^{II}.

** A system which is similar in some aspects to our own was previously proposed [11] for the process of the introduction of iron into the nucleus of mesoporphyrin ester.

*** A number of authors [12] consider that the main reaction which takes place as a result of the reaction of chlorophyll with $FeCl_3$ is the oxidation of the pigment. The conclusions of these authors which are based on experiments carried out in the presence of air, i. e., under conditions in which the main process taking place in these systems is retarded, are not convincing.

SUMMARY

1. The reaction of chlorophyll with ferric chloride in solutions of ether and acetone leads to the displacement of magnesium from the chlorophyll nucleus and the formation of pheophytin iron-III. The reaction takes place extremely slowly and is characterized by a high temperature coefficient.

2. In acetone solution the reaction takes place via a stage of the formation of an intermediate gray product having a spectrum which is characteristic of dihydroporphin derivatives. The addition of chlorides to a system containing this intermediate product leads to the regeneration of chlorophyll. The conversion of the intermediate gray product to pheophytin iron is an irreversible process.

3. Bivalent iron ions exert a marked catalytic influence on the process of the introduction of iron into the chlorophyll nucleus. Oxygen has an intense retarding effect on the reaction.

4. A system was proposed in which the principal role in the development of the reaction is played by the complex ions $Fe(MgPh)^{+++}$.

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FURTHER DISCUSSION

THE PROBLEM OF THE GENERAL DEFINITION OF CHEMISTRY*

Iu. A. Zhdanov

Our article [1] which led to a number of objections raised by Ia. E. Ekster [2] was published in the Journal of General Chemistry. We can only welcome the desire to clarify the main conceptions of chemical science in a discussion, but Ia. E. Ekster's objections are off the point and his own position seems somewhat contradictory.

We proposed the definition of chemistry as the science of the qualitative changes of bodies, taking place under the influence of changes in their quantitative composition and structure. Any formulation can, of course, be improved and corrected. Ekster supports us, pointing out the inadequacy of the famous definition of Engels (a definition adopted in a whole series of chemical and philosophical works published in this country).

In the final analysis the idea put forward by us amounts to the fact that the definition of chemistry must include the most important feature of chemism: the variation in the structure of substances. In this connection, structure is considered in the Butlerov sense as a stable order of reactions of atoms. The usual definition of chemistry as the science of substances and their changes does not contain this decisive factor and should, therefore, be corrected. This definition reflects the prestructural analytical stage in the development of chemistry.

On the one hand, Ekster objects to our criticism of the definition of chemistry as the science of substances and their changes, considering our proofs to be unconvincing. The fact cannot be escaped, however, that not all the changes of substances are of a chemical nature, in particular, for example, the processes of the transformation of the elements taking place on an enormous scale in the universe.

At the same time Ekster, on the other hand, favors our definition affirming that "the chemical structure of a substance is that inalienable quality which determines its chemical behavior." It is remarkable that having written this, Ekster describes the inclusion of the "inalienable quality" in the definition of chemism as to some extent tautological. In such a case any definition of any concept must be considered tautological, including the definition of chemistry as the science of substances and their changes. Surely it is clear that in the formulation of the general definition of chemistry the basis taken must be that inalienable quality which determines the chemical behavior of substances. Ekster's other objections are not a matter of principle but it is worthwhile, however, to deal with them.

Ekster objects to the term "body" as applied to chemical substances. This term seems reasonably satisfactory to us. Many chemists have employed it successfully, including Berzelius and Butlerov (to mention only his famous definition of the significance of rational formulas: "For each body there will be only one rational formula possible and when the general laws of the relationship between the chemical properties of bodies and their chemical structure becomes known a similar formula will express all these properties").

Ekster further maintains that our proposed definition of chemism excludes from consideration the phenomena of isomerism. This is an obvious misunderstanding. It will be clear to anyone who reads our article carefully that it was precisely the phenomenon of isomerism which was the initial point for the criticism of the analytical definition of the subject of general chemistry. But if we maintain the formal point of view adopted by Ekster it must be pointed out that in the words "composition and structure" the conjunction "and" can have a separating as well as a connecting meaning. When we say that sodium has the capacity to combine with chlorine and bromine, an informed man will hardly think that sodium cannot combined with each of the halogens separately. The word "or" can, of course, be put in brackets at the side of "and" but this does not alter the essence of the matter.

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* Reply to Ia. E. Ekster.

As regards Ekster's remark to the effect that when chemical changes take place, some qualitative indices always undergo a change, is, of course, correct. The point dealt with in Engels' definition is, however, the number of atoms in molecules which remain unchanged in isomeric changes.

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* Original Russian pagination. See C. B. pagination.

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THE PROPERTIES OF SALT–FORM COMPOUNDS OF VARIABLE COMPOSITION AND VIEWS ON THEIR CHEMICAL STRUCTURE

S.M. Ariia and M.P. Morozova

In connection with the problem of whether a chemical compound has an inherently fixed or variable composition, for compounds in which appreciable deviations from a stoichiometric composition are possible, the range of these deviations is one of the most important problems of general chemistry.

The work of N.S. Kurnakov is of decisive significance in the development of this problem, having an enormous effect on contemporary ideas about chemical combination. The subsequent emergence and rapid development of the x-ray diffraction method of investigating solid bodies made possible an approach to an understanding of the views put forward by N.S. Kurnakov with regard to structural ideas.

The experience accumulated in the course of x-ray crystallographic investigations was generalized by the efforts of a whole series of chemical crystallographers. It was noted that compounds of variable composition (CVC's) consist of subtraction, interstitial or substituted lattices [1-8].

These aspects constitute the basis on which the investigation of CVC's is being developed (the thermodynamics of CVC's are studied quite inadequately). Such typical CVC's as ferrous oxide FeO_{1+x}, titanous oxide $TiO_{1\pm x}$ and vanadous oxide $VO_{1\pm x}$, are considered as defective structures of the NaCl type, namely subtractive lattices based on this structure. It is considered that in the general case both in the metal-atom and in the oxygen-atom sub-lattice there is a certain proportion of vacant positions (differing in the two sub-lattices). The electroneutrality of the lattices requires the presence in the metal-atom sub-lattice of atoms in a valence state differing from that of the majority. In these circumstances the distribution of both these atoms and the vacant positions in the lattice is uniform and generally statistically disordered.

The problem of the present paper is the examination of the form of the relationship between certain properties, in the first case the thermodynamic characteristics, and composition of some binary systems containing CVC's.

1. Enthalpy of Formation, Gram-Formula Volume, Entropy

In all cases so far examined, the enthalpy of formation of oxides of variable composition (FeO_{1+x} [9], TiO_{1+x} [10], VO_{1+x} [11]) is a linear function of composition. Moreover, the enthalpy of formation of the substances lies within the limits of the region of homogeneity and is practically equal to the enthalpy of formation of a mixture of the same empirical composition of certain compounds of the corresponding systems. Thus, the enthalpies of formation of substances of the composition $TiO_{1.00}$–$TiO_{1.20}$, $VO_{1.00}$–$VO_{1.27}$ or $FeO_{1.04}$–$FeO_{1.11}$ ($TiO_{1.20}$, $VO_{1.27}$, $FeO_{1.11}$ – the upper boundaries of the region of homogeneity) coincide very accurately with the enthalpies of formation of mixtures of the same empirical composition of the oxides $MeO_{1.00}$ and $MeO_{1.50}$.

The enthalpy of formation of substances lying within the composition interval $TiO_{1.00}$ and $TiO_{0.80}$ (the lower boundary of the region of homogeneity of titanous oxide) is close to the enthalpy of formation of a mixture of $TiO_{1.00}$ and $TiO_{0.48}$ (the upper boundary of the region of homogeneity of the compound lowest in oxygen in the system Ti–O).

The relationships recorded are given in Figs. 1-3.

The generally known fact that the enthalpy of polymorphic transformation of binary compounds is rather small in absolute magnitude, indicates that the relationship between enthalpy of formation (which is in principle a structure-dependent magnitude) and type of lattice is not very significant.

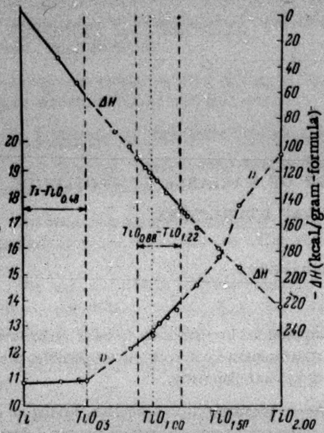

Fig. 1. Variation of enthalpy of formation (in kcal per gram-formula) and gram-formula volume (in cm³) of titanium oxides with composition.

At the same time, the enthalpies of formation of those discrete compounds of the elements of the transition groups in which these elements act in two different valence states differ rather appreciably from the enthalpies of formation of a mixture, of the same empirical composition, of those compounds in each of which the element of the transition group acts only in one of the two valence states which coexist in the lattice of a mixed compound (thus the heat of formation of $MnO_{1.33}$ is 3.6 kcal greater than the heat of formation of a mixture of $MnO_{1.00}$ and $MnO_{1.50}$ of the same empirical composition [12] and the heat of formation of $WO_{2.67}$ is 2.5 kcal less than the heat of formation of a mixture of WO_2 and WO_3 of the same empirical composition). Thus, the relationship of the change of enthalpy of formation of some CVC's with composition is not a simple effect, as for example, in the FeO_{1+x} lattice where the iron occurs in the same valence states, being in the forms $FeO_{1.00}$ and $FeO_{1.50}$.

The equality of the enthalpy of formation of substances lying within the limits of the region of homogeneity and the enthalpy of formation of mixtures, of the same empirical composition, of certain specific compounds of the corresponding system is undoubtedly a consequence of the structural peculiarities of the lattices of such CVC's.

According to the classical structural model of CVC's, in the MeO_{1+x} lattice the atoms of Me^{III} and the vacant positions are distributed uniformly and in statistical disorder. In this case Madelung's constant would have been different from that for a mixture of the $MeO_{1.00}$ and $MeO_{1.50}$ lattices and, correspondingly, the electrostatic interaction energy in the MeO_{1+x} lattice must differ from the electrostatic interaction energy in a mixture of $MeO_{1.00}$ and $MeO_{1.50}$.

In the $MeO_{1.00}$ and $MeO_{1.50}$ lattices the Me^{II} and Me^{III} atoms occur in a state of specific exchange interaction (this is shown, in particular, by the magnetic properties of compounds of elements of the transition groups) which introduces a definite component into the energy of the lattice and consequently also to the enthalpy of formation.

In MeO_{1+x}, according to the classical structural model, the atoms of Me^{III}, while being uniformly distributed, are placed far apart (for example, in the composition $MeO_{1.05}$); consequently, the exchange interaction between them is hindered and must be superseded in the main by the interaction between Me^{III} and Me^{II} which is characterized by another energy effect.

It would seem that this fact also must require an enthalpy of formation differing from the enthalpy of formation of a mixture of $MeO_{1.00}$ and $MeO_{1.50}$ of the same empirical composition, for substances lying within the limits of the region of homogeneity.

Figure 2, which illustrates the variation of the enthalpy of formation in the system Fe–O, incidentally gives rise to the following consideration. The heat of formation of $FeO_{1.33}$ is appreciably greater than the heat of formation of a mixture of $FeO_{1.00}$ and $FeO_{1.50}$, evidently because of the uniform distribution of Fe^{II} and Fe^{III} atoms in the lattice which obviously occurs in a condition of special, specific interaction.

If such a uniform distribution of Fe^{II} and Fe^{III} had taken place in the FeO_{1+x} lattice, then probably the enthalpy of formation of the substance of composition FeO_{1+x} would have been near to that of a mixture of $FeO_{1.00}$ and $FeO_{1.33}$ and not of a mixture of $FeO_{1.00}$ and $FeO_{1.50}$, which, in fact, occurs. It seems to us that the zero enthalpy of mixing of $FeO_{1.00}$ and $FeO_{1.50}$ on formation of FeO_{1+x} can be considered as an indication that in this

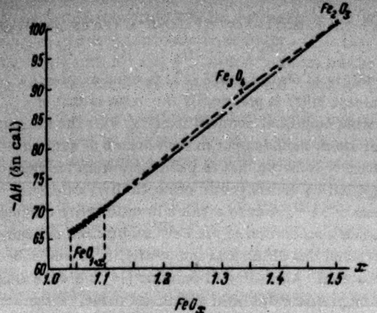

Fig. 2. Variation of enthalpy of formation of iron oxides (in kcal per gram-formula) with composition of the oxides.

case the classical model of a CVC lattice is not formed, but a submicro-inhomogeneous structure arises — the $FeO_{1.00}$ lattice in which islands of agglomerates of Fe^{III} are disseminated (in conjunction, of course, with atoms of oxygen in the appropriate ratio).

In the light of what has been said above it is obvious that the practical equality of the enthalpy of formation of substances lying within the region of homogeneity to that of mixtures of the corresponding compounds of the same empirical composition must be in accordance with such a submicro-inhomogeneous structure. It is evident that the proximity of the gram-formula volumes of substances lying within the region of homogeneity to that of mixtures of the corresponding compounds must also be in accordance with the submicro-inhomogeneous structure of lattices of CVC's.

As is seen from Fig. 1, this actually occurs in the system Ti−O [13]. The gram-formula volume of VO_{1+x} is a little smaller than that of a mixture of $VO_{1.00}$ and $VO_{1.50}$ of the same empirical composition.

The reason, at least in part, is that it cannot, of course, be assumed in principle that all the Me^{III} atoms in the Me_{1+x} lattice, without exception, enter into the composition of their agglomerates. A certain proportion of the Me^{III} atoms (we will discuss this in detail below) must occur "one by one" within the limits of the basic lattice, which cannot but give rise to the known deviation of certain properties from additivity.

The entropy of ferrous oxide, FeO_{1+x} as a function of composition is shown in Fig. 4. It is clearly evident that it is greater than the entropy of a mixture of $FeO_{1.00}$ and $FeO_{1.50}$ of the same empirical composition. This fact is also responsible for the possibility of a thermodynamically stable state of homogeneous (in the ordinary sense) substances of the composition FeO_{1+x} in comparison with a mixture of $FeO_{1.00}$ and $FeO_{1.50}$ and even in comparison with a mixture of $FeO_{1.00}$ and $FeO_{1.33}$ (Fe_3O_4).

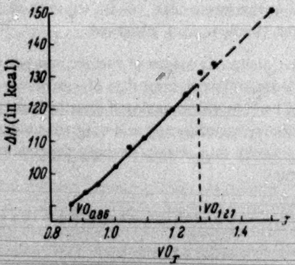

Fig. 3. Variation of enthalpy of formation of vanadium oxides (in kcal per gram-formula) with composition of the oxides.

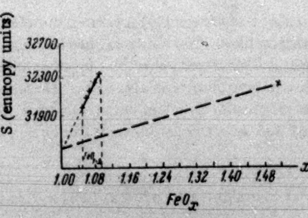

Fig. 4. Variation of entropy of iron oxides (in entropy units) with composition of the oxides at 1104°K.

It should be noted that the submicro-inhomogeneous lattice that we postulate for certain CVC's must behave thermodynamically as a single phase since the agglomerates of Me^{III} atoms cannot be regarded as independent formations. Because of the low values of their numbers, interactions of their component Me^{III} atoms and the atoms of the nonmetallic element with the particles of the basic lattice are of great significance. The submicro-inhomogeneous structure in question is by no means equivalent to a mechanical mixture of the corresponding compounds.

2. The Magnetic Susceptibility and Electrical Conductivity of Iron Oxides at High Temperatures

As has been shown previously [14] the magnetic susceptibility of ferrous oxide at high temperatures is a linear function of composition. Furthermore, the magnetic susceptibility is practically the same as that of a mixture of low-oxygen ferrous oxide and ferric oxide, of the same empirical composition (Fig. 5). The magnetic susceptibility of $FeO_{1.50}$ (Fe_2O_3) is considerably lower than that which should occur in the absence of antiferromagnetic interaction between the Fe^{III} atoms. At the same time it is known that in going over from the Fe_2O_3 to the $Fe_2(SO_4)_3$ lattice the magnetic susceptibility, calculated on 1 gram-atom of Fe^{III}, rises to a value in conformity with the ionic model since a separation of the Fe^{III} atoms from one another takes place and this eliminates the possibility of antiferromagnetic interaction. According to Selwood [15] the same thing occurs on diluting ferric oxide with aluminum oxide. If the FeO_{1+x} lattice were characterized by the uniform distribution of Fe^{III} atoms in it, it would seem that the antiferromagnetic interaction between the Fe^{III} atoms even in this case, should be weakened to a considerable extent, because even at a composition of $FeO_{1.10}$ there are four atoms of Fe^{II} to one atom of Fe^{III}, i.e., the Fe^{III} atoms should be sufficiently separated from one another.

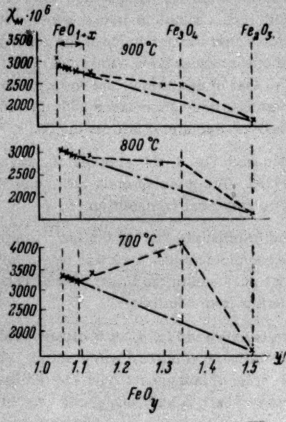

Fig. 5. Variation of magnetic susceptibility of iron oxides with composition at high temperatures.

In the light of this it can be surmised that the equality of the magnetic susceptibility of FeO_{1+x} to that of a mixture of $FeO_{1.00}$ and $FeO_{1.50}$ of the same empirical composition indicates that segregation of the Fe^{III} atoms, and not a uniform distribution of these in the lattice, takes place. It should also be noted that the $FeO_{1.33}$ lattice, in which the Fe^{III} and Fe^{II} atoms are distributed uniformly, is characterized, as is known, by ferromagnetic properties. It can be surmised that if such a distribution, postulated by the classical model of CVC lattices, should occur in FeO_{1+x} the latter should have had, if only in embryo, elements of this ferromagnetic interaction. The magnetic susceptibility of FeO_{1+x} should approximate that of a mixture of $FeO_{1.00}$ and $FeO_{1.33}$, which is not, in fact, observed.

Aubry and Marion [16] measured the electrical conductivity of ferrous oxides of various compositions at high temperatures. The electrical conductivity of FeO_{1+x} differs qualitatively from that of a mixture of $FeO_{1.00}$ and $FeO_{1.50}$. We stated above that together with agglomerates of Fe^{III} atoms an isolated distribution of these (and vacant positions) must also occur. On such properties as enthalpy of formation and magnetic susceptibility this has practically no effect, but on electrical conductivity – a property that is very strongly dependent on "impurities" and defective lattices – it can have a very marked effect.

3. Statistical-Thermodynamic Examination of the Problem of the Chemical Structure of Compounds of Variable Composition

Let us suppose that in the system A–B there are stoichiometric compounds $AB_{1.00}$ and $AB_{1.50}$ and let us suppose that there is a region of homogeneity from the composition $AB_{1.00}$ to AB_{1+x} ($1 + x < 1.5$, B is a divalent element). If the CVC $AB_{1.00}$–AB_{1+x} has the structure specified by the classical model, and at the same time substances of a composition included in this interval are formed from $AB_{1.00}$ and $AB_{1.50}$ without change in enthalpy, as occurs in a number of cases mentioned above, then their thermodynamic stability is determined by their greater entropy value with respect to a mixture of $AB_{1.00}$ and $AB_{1.50}$. This increased entropy is explained by an increased number of micro states brought about by different possibilities of substitutions of the vacant positions in the lattice.

If AB_{1+x} is formed endothermically from $AB_{1.00}$ and $AB_{1.50}$, then the classical model of the structure of the AB_{1+x} lattice must correspond to a higher entropy value because the vibrational frequencies of the atoms change correspondingly. However, if the endothermal effect is sufficiently great in its absolute magnitude the classical model lattice formation will be thermodynamically unfavorable because the increase in entropy will not be compensated by an increase in enthalpy. This case occurs, in particular, when the specific exchange interaction of A^{II} with A^{II} and A^{III} with A^{III} atoms results in a more significant lowering of the energy of the system than does the exchange interaction of A^{II} with A^{III}.

In this case a lattice of submicro-inhomogeneous structure can arise which, as stated above, under certain conditions can be formed from $AB_{1.00}$ and $AB_{1.50}$ with a practically zero heat effect.* At the same time, because the postulated agglomerates of A^{III} atoms cannot necessarily be considered as stable formations, but rather as continuously forming and disrupting formations of submicro-inhomogeneous structure, there must also be a concomitant increase in entropy. As a rule, the structure $AB_{1.50}$ can be obtained from the structure $AB_{1.00}$ by removing from the latter a definite proportion of A atoms (if close packing of B atoms forms the basis of both structures) with corresponding, simultaneous changes in the grouping of the component particles. In the light of this, in the A^{III} agglomerate region, in comparison with the $AB_{1.00}$ structure, there are vacant positions which, as a result of the dynamic nature of the A^{III} atom agglomerates, can also be distributed variably in the lattice: a vacant position can occur at any point in the A-atom sub-lattice. Correspondingly, also in the case of formation of a submicro-inhomogeneous lattice from $AB_{1.00}$ and $AB_{1.50}$, an increase in entropy must occur.**

A conclusion on the possibility of the agglomeration of A^{III} atoms in the AB_{1+x} lattice in the case when the latter is formed from $AB_{1.00}$ and $AB_{1.50}$ without change in enthalpy, can be arrived at by examining this question from the point of view of the fluctuation theory.

Let us assume (though this is very improbable, as we have stated above) that the AB_{1+x} lattice with a uniform distribution of A^{III} atoms and vacant positions is formed from $AB_{1.00}$ and $AB_{1.50}$ without change in enthalpy. Obviously, in this case a lattice of submicro-inhomogeneous structure should be formed (more probably) without change in enthalpy. In accordance with this the occurrence of agglomerates of A^{III} atoms in the AB_{1+x} lattice in the form of fluctuations must be accompanied by a practically zero change in enthalpy and a certain decrease in entropy, i.e., it must be accompanied by an insignificant increase in thermodynamic potential and this is just the right condition for a high probability for such fluctuations to occur.

It is appropriate to note in this connection that the assumption of the necessity of fluctuations of concentration in liquid solutions was used very fruitfully by M.I. Shakhparonov [17, 18].

The submicro-inhomogeneous structure of CVC lattices and the uniform distribution therein of atoms not in the principal valence state of the majority, and of vacant positions, should be regarded as two extreme types of chemical structure of such compounds. In an actual CVC lattice, submicro-inhomogeneous elements, segregation of A^{III} atoms and isolated distribution of these in the lattice must all occur.

The extent to which the structure of a given CVC approximates one of these extreme types must depend, above all, on the nature of the compound and also on temperature and the magnitude of the deviation of the compound from a stoichiometric composition. An increase in the extent of the deviation from a stoichiometric composition should draw the lattice structure toward the extreme case of a submicro-inhomogeneous structure; an increase in temperature should act in the opposite direction.

In the systems metal–carbon [19], metal–sulphur, metal–metal [20] other relationships between change in enthalpy of formation and other properties of the CVC's with composition are observed; it can be surmised accordingly that submicro-inhomogeneous elements enter into their lattices to a lesser extent. It is without doubt, however, that there must be submicro-inhomogeneous elements, particularly near the upper boundary of the region of homogeneity.

What is the structure in the region of agglomerates of A^{III} atoms in the AB_{1+x} lattice? Is it the same as that of the compound $AB_{1.50}$, or, in spite of the segregation of A^{III} atoms everywhere, is the same $AB_{1.00}$ structure maintained in all lattices?

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*It is quite clear that not all compounds of $AB_{1.00}$ and $AB_{1.50}$ can form such submicro-inhomogeneous lattices isoenthalpically. This is possible only for a certain relationship of the structures of $AB_{1.00}$ and $AB_{1.50}$, the characteristics of which are as yet unknown.

**It will be lower than in the case of uniform, statistically disordered distribution of vacant positions because in the case of the segregation of A^{III} the distribution of individual vacant positions does not take place independently of one another.

It will not be possible to draw any reliable conclusions in this direction until experimental data are available. Furthermore, it is clear that the outline of the chemical structure of CVC's postulated still needs careful verification by a whole series of experimental methods.

SUMMARY

Examination of the nature of the variation of certain properties with composition in binary systems of compounds of variable composition and also a statistical-thermodynamic examination of the question of the chemical structure of compounds of variable composition, lead to the conclusion that in the lattices of the latter, segregation of atoms of the transition groups, that are in different valence states, occurs to some degree or other.

In other words, the lattices of compounds of variable composition, in a number of cases can have a submicro-inhomogeneous structure (while remaining as a single phase in the thermodynamic sense).

The proportion of elements of submicro-inhomogeneous structure must depend on the nature of the compound, on temperature and on the degree of deviation of the CVC from a stoichiometric composition.

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STUDY OF DOUBLE SULFATES OF AMERICIUM BY ABSORPTION SPECTRA IN CRYSTALS

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In this work the ordinary sulfate of americium and its double sulfates with potassium, thallium, rubidium and cesium were studied. The ordinary sulfate and the following double sulfates of americium were identified as:

$Am_2(SO_4)_3 \cdot 5H_2O$

$KAm(SO_4)_2 \cdot 2H_2O$
$TlAm(SO_4)_2 \cdot 4H_2O$
$RbAm(SO_4)_2 \cdot 4H_2O$
$CsAm(SO_4)_2 \cdot 4H_2O$

$K_3Am(SO_4)_3 \cdot H_2O$

$K_8Am_2(SO_4)_7$
$Tl_8Am_2(SO_4)_7$
$Cs_8Am_2(SO_4)_7$

The absorption spectra of polycrystalline samples of the compounds were investigated in the region 4000 to 8500 A at 300, 200 and 80°K. The peak separation of the electronic bands of Am^{+++} in the 5000 A region was examined and the electronic-vibrational "lines" for the compounds in question in the 4500 A region were identified. The effect of water of crystallization on the nature of the peak separation of the 5000 A electronic bands and on the nature of the electronic-vibrational "lines" in the 4500 A region was examined.

It is known that the double sulfates of rare earth elements and alkali metals have poor solubility and as a consequence of this they play an important role in the analytical chemistry of these elements. In conformity with the actinide theory, the transuranium elements are analogous to the rare earth elements and a number of their compounds have similar chemical properties, in particular, the similarity of the double sulfates with alkali metals.

There are data in the literature about identified double sulfates of neodymium with potassium, sodium and ammonium [1] and double sulfates of cerium and samarium with sodium [2].

Of the double sulfates of the transuranium elements with alkali metals, the system $R_2SO_4 - Pu_2(SO_4)_3 - H_2O$ (where R = K, Tl, Rb or Cs) has been studied most fully [1]. From the example of the systems of the double sulfates of Pu and Nd, the similarity of this class of actinide compound with the corresponding lanthanide compounds was demonstrated; in particular, the isomorphism of $NaPu(SO_4)_2 \cdot H_2O$, $KPu(SO_4)_2 \cdot 2H_2O$, $NH_4Pu(SO_4)_2 \cdot 4H_2O$ with the analogous neodymium compounds was shown by the results of x-ray structural analysis [1].

Similarity of the spectra of hydrated ions of the actinides and lanthanides was shown by investigations on the spectrophotometry of solutions of the actinide compounds, these spectra being characterized by narrow, sharp absorption bands in the ultraviolet, visible and near-infrared regions. This similarity, which is connected with the presence in the elements of both families of completed f-electron shells, enables an analysis of the relationships characteristic of the spectra of f-elements in crystals to be made on the example of the lanthanides, the literature on which is quite voluminous.

The appearance of structure in the absorption bands of lanthanides in crystals (noted by many authors [3-8]) indicates that in the crystal an absorbing ion falls within the sphere of action of fields created by the association of charges entering into the crystal lattice. This brings about a splitting of energy levels of the ion into a number of components and a group of "lines" appears which corresponds to exchange between the components of the separated energy levels. On the basis of the observed structure of the absorption bands brought about by electronic transitions, an idea can be obtained about the electrical fields in the crystal lattice which enable the f-element ions to be used as optical probes in crystals.

In the spectrum of neodymium salts, Ewald [3] discovered a group of weak, sharp "lines" with spacings of some hundreds of cm^{-1} on the shortwave side of each electronic band.

Accurate measurements of the frequency difference showed their coincidence with the natural vibrational frequencies of ions and polar molecules, known from the data of Raman and vibrational infrared spectra. These "lines" were identified as electronic-vibrational lines arising from the superposition of lattice vibrations on the electronic transitions. These "lines" were shown to be very sensitive to isomorphic change of the lattice components.

This effect should appear to a very marked extent in the case of $5f$-elements because the $5f$-shell is energetically and spatially more subject to external electrical action than the $4f$-shell of lanthanides. This property makes actinide ions still more suitable for the study of the internal nature of crystals.

Data on the absorption spectra of actinide compounds in crystals are few and are of a qualitative nature. The absorption spectra of UCl_3, $NpCl_3$, $PuCl_3$ and $AmCl_3$ have been investigated in comparison with the spectrum of $NdCl_3$ for the purpose of drawing an analogy with the lanthanides [9]. The absorption spectra of crystals of UF_4 and of the double fluorides of U (IV) with sodium and potassium have been described [10], and on the basis of the similarity of the absorption spectra it was concluded that these compounds are isomorphic. The absorption spectrum of $AmCl_3 \cdot H_2O$ has also been studied [11].

EXPERIMENTAL

Preparation and Analysis of the Ordinary and Double Sulfates of Americium With Potassium, Thallium, Rubidium and Cesium

The isotope Am^{241} was used for the preparation of all the compounds. The ordinary sulfate of americium was prepared by dissolving the dioxide AmO_2, obtained by calcination of the hydroxide $Am(OH)_3$ at 750-850°, in 8 M H_2SO_4. The solution was diluted to an acidity of 0.5 M H_2SO_4 and ethanol was added until a precipitate separated. The precipitate was removed, washed three times with ethanol and dried in vacuo to constant weight at 20°.

For the preparation of the double sulfates of americium with potassium, thallium, rubidium and cesium, different volumes of standard solutions of the ordinary sulfates of the metals were added to the solution of $Am_2(SO_4)_3$ at an acidity of 0.5 M H_2SO_4, such as to give the different ratios of $M_{R^+}/M_{Am^{+++}}$. For low molar ratios of $M_{R^+}/M_{Am^{+++}}$, in order to accelerate the precipitation of the correspondingly little-soluble double sulfates, ethanol was added in the ratio 1/20, by volume. The precipitates obtained were separated, washed four times with 50% ethanol in 0.1 M H_2SO_4, twice in 50% methanol in 0.1 M H_2SO_4 and dried in vacuo to constant weight at 20°.

The air-dried precipitates were analyzed for their contents of americium, SO_4^{--} and water. Americium was determined radiometrically in a slit ionization chamber filled with argon, and by a gravimetric method as AmO_2. The SO_4^{--} ion was determined gravimetrically as $BaSO_4$. Water was determined by the difference between the weight of the air-dried precipitate and that of the precipitate after calcining at 350-400°. In the case of the double potassium-americium sulfates, a colorimetric analysis for potassium as the dipicrylaminate [12] was also carried out.

The ordinary sulfate and the double potassium-americium sulfates. From the analytical data the formula $Am_2(SO_4)_3 \cdot 5H_2O$ was assigned to the ordinary americium sulfate prepared by the method described above.

A phase diagram was plotted for the system $K_2SO_4-Am_2(SO_4)_3-H_2O$ in the region of $M_{K^+}/M_{Am^{+++}}$ from 3.0 to 418.0 and the following compounds were identified:

$KAm(SO_4)_2 \cdot 2H_2O$	$M_{K^+}/M_{Am^{+++}}$ from 3.7 to 10.0
$K_3Am(SO_4)_3 \cdot H_2O$	$M_{K^+}/M_{Am^{+++}}$ from 10.3 to 37.9
$K_8Am_2(SO_4)_7$	$M_{K^+}/M_{Am^{+++}}$ from 43.0 to 418.0

The phase diagram of the system $K_2SO_4-Am_2(SO_4)_3-H_2O$ is given in Fig. 1. Analytical data for the ordinary sulfate and for the double sulfates of americium with potassium are set out in Table 1. In Table 2 data are given on the determination of the solubility of the double potassium-americium sulfates.

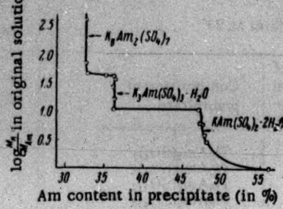

Fig. 1. Phase diagram of the system $K_2SO_4-Am_2(SO_4)_3-H_2O$.

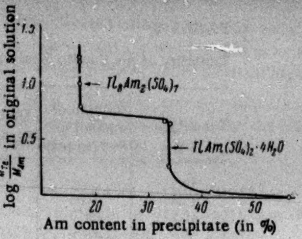

Fig. 2. Phase diagram of the system $Tl_2SO_4-Am_2(SO_4)_3-H_2O$.

TABLE 1

Analysis of the Single Sulfate and Double Potassium-Americium Sulfates

Compound	K content (%)		Am content (%)		SO_4^{--} content (%)		H_2O content (%)	
	found	calc.	found	calc.	found	calc.	found	calc.
$Am_2(SO_4)_3 \cdot 5H_2O$	—	—	56.1±0.2	56.0	33.5 ± 0.5	33.5	10.4±0.2	10.4
$KAm(SO_4)_2 \cdot 2H_2O$	—	7.7	47.4±0.3	47.4	—	37.8	7.2±0.2	7.1
$K_3Am(SO_4)_3 \cdot H_2O$	18.3	17.6	36.3±0.2	36.3	41.7	43.3	2.5	2.7
$K_8Am_2(SO_4)_7$	20.9	21.3	32.8±0.2	32.8	46.0	45.8	—	—

TABLE 2

Solubility of the Double Potassium-Americium Sulfates at 20°

$M_{K^+}/M_{Am^{+++}}$	Volume of ethanol added (in ml)	Solubility (g Am/liter)	Content of americium in precipitate (in %)	Composition of precipitate
418.0	0.20	0.003	32.8	$K_8Am_2(SO_4)_7$
73.5	—	0.014	32.8	$K_8Am_2(SO_4)_7$
48.5	—	0.030	33.0	—
45.5	—	0.020	35.3	—
43.2	—	0.020	36.2	—
37.9	—	0.040	36.4	$K_3Am(SO_4)_3 \cdot H_2O$
27.3	—	0.050	36.1	$K_3Am(SO_4)_3 \cdot H_2O$
17.0	—	0.120	36.2	$K_3Am(SO_4)_3 \cdot H_2O$
10.0	0.03	0.160	36.3	—
6.4	0.03	2.800	47.2	$KAm(SO_4)_2 \cdot 2H_2O$
6.3	—	—	47.5	$KAm(SO_4)_2 \cdot 2H_2O$
3.7	0.02	3.800	47.7	$KAm(SO_4)_2 \cdot 2H_2O$
3.0	0.02	—	48.0	$KAm(SO_4)_2 \cdot 2H_2O$

Double thallium-americium sulfates. A phase diagram was plotted for the system $Tl_2SO_4-Am_2(SO_4)_3-H_2O$ in the region of $M_{Tl^+}/M_{Am^{+++}}$ from 1.1 to 17.3 and the individual compounds $TlAm(SO_4)_2 \cdot 4H_2O$ and $Tl_8Am_2(SO_4)_7$ were identified.

These compounds were prepared by a method similar to that described above for the double potassium-americium sulfates.

The phase diagram of the system $Tl_2SO_4-Am_2(SO_4)_3-H_2O$ is shown in Fig. 2.

TABLE 3

Solubility of the Double Thallium-Americium Sulfates at 20°

$M_{Tl^+}/M_{Am^{+++}}$	Volume of ethanol added (in ml)	Solubility (g Am/liter)	Content of americium in precipitate (in %)	Composition of precipitate
17.3	—	1.40	17.3	$Tl_8Am_2(SO_4)_7$
15.8	0.08	1.30	17.3	$Tl_8Am_2(SO_4)_7$
10.9	0.10	2.20	17.3	$Tl_8Am_2(SO_4)_7$
6.3	0.06	4.20	17.4	$Tl_8Am_2(SO_4)_7$
4.8	0.06	—	33.2	—
4.5	0.04	4.60	34.2	$TlAm(SO_4)_2 \cdot 4H_2O$
1.9	0.03	5.70	33.9	$TlAm(SO_4)_2 \cdot 4H_2O$
1.1	0.03	6.00	40.8	—

TABLE 4

Comparison of the Ordinary Sulfate and Double Sulfates of Plutonium With the Corresponding Americium Compounds

Plutonium compounds	Americium compounds
$Pu_2(SO_4)_3 \cdot 5H_2O$	$Am_2(SO_4)_3 \cdot 5H_2O$
$Pu_2(SO_4)_3 \cdot 7H_2O$	He found
$KPu(SO_4)_2 \cdot 2H_2O$	$KAm(SO_4)_2 \cdot 2H_2O$
$KPu(SO_4)_2 \cdot H_2O$	He found
He found	$K_3Am(SO_4)_3 \cdot H_2O$
$K_8Pu_2(SO_4)_7$	$K_8Am_2(SO_4)_7$
$TlPu(SO_4)_2 \cdot 4H_2O$	$TlAm(SO_4)_2 \cdot 4H_2O$
$RbPu(SO_4)_2 \cdot 4H_2O$	$RbAm(SO_4)_2 \cdot 4H_2O$
$CsPu(SO_4)_2 \cdot 4H_2O$	$CsAm(SO_4)_2 \cdot 4H_2O$

In Table 3 results of the determination of the solubility of the double thallium-americium sulfates are given.

Double sulfates of americium with rubidium and cesium. A phase diagram was plotted for the system $Rb_2SO_4-Am_2(SO_4)_3-H_2O$ in the region of $M_{Rb^+}/M_{Am^{+++}}$ from 0.6 to 325.3 and a double sulfate of the composition $RbAm(SO_4)_2 \cdot 4H_2O$ was identified. No phase diagram was plotted for the system $Cs_2SO_4-Am_2(SO_4)_3-H_2O$. Two double sulfates were obtained that precipitated at the $M_{Cs^+}/M_{Am^{+++}}$ ratios of 51.7 and 129.1. For the compound obtained at the ratio $M_{Cs^+}/M_{Am^{+++}}$ of 51.7 the composition $CsAm(SO_4)_2 \cdot 4H_2O$ was found. The compound obtained at the ratio $M_{Cs^+}/M_{Am^{+++}}$ of 129.1 was not analyzed. The absorption spectrum of this double sulfate was recorded and the composition $Cs_8Am_2(SO_4)_7$ was assigned to this compound on the basis of the spectrographic data.

The following conclusions can be drawn from the analytical data and from the solubilities of the americium double sulfates identified.

1. The americium double sulfates have low solubility.

2. In the series of double sulfates of americium with potassium and thallium, the solubility decreases with increasing content of the monovalent cation: for the double sulfates with potassium from 3.80 to 0.003 g Am/liter, for the double sulfates with thallium from 6.00 to 1.40 g Am/liter.

3. The double thallium-americium sulfates have greater solubility than the corresponding double potassium-americium sulfates.

4. A double sulfate of the composition $R_3Am(SO_4)_3 \cdot H_2O$ was identified only in the case of potassium.

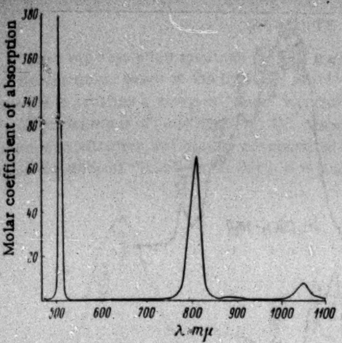

Fig. 3. Absorption spectrum of Am^{+++} in 0.2 M $HClO_4$.

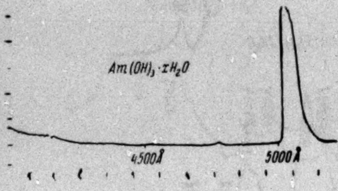

Fig. 4. Absorption spectrum of $Am(OH)_3$ in the region 4000-5200 A at 80°K.

5. The double thallium-americium sulfates are formed at lower molar ratios of $M_{R^+}/M_{Am^{+++}}$ than the analogous double potassium-americium sulfates.

In Table 4 the known ordinary sulfates and double sulfates of plutonium are compared with the corresponding americium compounds studied by us.

Absorption Spectra of the Ordinary Sulfate and Double Sulfate of Americium With Potassium, Thallium and Cesium

The hydrated Am^{+++} ion is characterized by the occurrence of a small number of sharp, intense absorption bands widely separated from one another (5030, 8110 and 10500 A). The absorption spectrum of Am^{+++} in 2 M $HClO_4$ [13] is shown in Fig. 3. The comparative simplicity of the absorption spectrum of hydrated Am^{+++} makes this ion particularly suitable for the study of the absorption spectra of Am^{+++} compounds in crystals because it would be expected that electronic absorption bands in crystals will undergo specific peak separation and electronic-vibrational absorption bands will be uncovered which would be extremely difficult to interpret in the case of hydrated-ion absorption spectra of a complex nature.

In the present work the absorption spectra of the following compounds were plotted:

$Am_2(SO_4)_3 \cdot 5H_2O$
$Am_2(SO_4)_3$

$KAm(SO_4)_2 \cdot 2H_2O$
$KAm(SO_4)_2$
$TlAm(SO_4)_2 \cdot 4H_2O$
$CsAm(SO_4)_2 \cdot 4H_2O$

$K_3Am(SO_4)_3 \cdot H_2O$

$K_8Am_2(SO_4)_7$
$Tl_8Am_2(SO_4)_7$
$Cs_8Am_2(SO_4)_7$

The anhydrous compounds $Am_2(SO_4)_3$ and $KAm(SO_4)_2$ were prepared by calcining the corresponding hydrated crystals at 350-400°. The method of preparing the samples for plotting absorption spectra was determined mainly by the necessity for deep cooling of the specimens during the plotting and for maintaining an approximately constant film thickness. The following method was worked out for the preparation of the specimens: between two flat, glass plates of 32 mm diameter, and 1 mm thickness is placed a "cambric cloth" washer of the same diameter and 0.12 mm thick with a central aperture of 5 mm diameter. In the space between the glass plates formed by this aperture, 4-5 mg of the crystals of the compound being investigated are placed and the glass plates are held together by a thin rubber ring. The whole system, together with a diaphragm of nonactinic paper of 5 mm diameter, was fixed in a special clamp and for low-temperature plots was lowered on an overhead support into a transparent Dewar vessel containing a cooling mixture. Two types of samples were used for examination – undiluted and diluted with fused potassium sulfate. Weak "lines" were plotted with undiluted samples, the specimens diluted with potassium sulfate were used for plotting the intense absorption bands.

Preliminary plots showed that dilution of the specimens with potassium sulfate does not alter the character of the spectrum but it lowers the absorption in the region of the intense bands sufficiently to enable the fine structure to be seen.

The absorption spectra were plotted on an ISP-51 three-prism, glass spectrograph with a camera of F = 270 mm, in the wavelength region from 4000 to 8500 A. The degrees of dispersion of the apparatus for the respective wavelengths were:

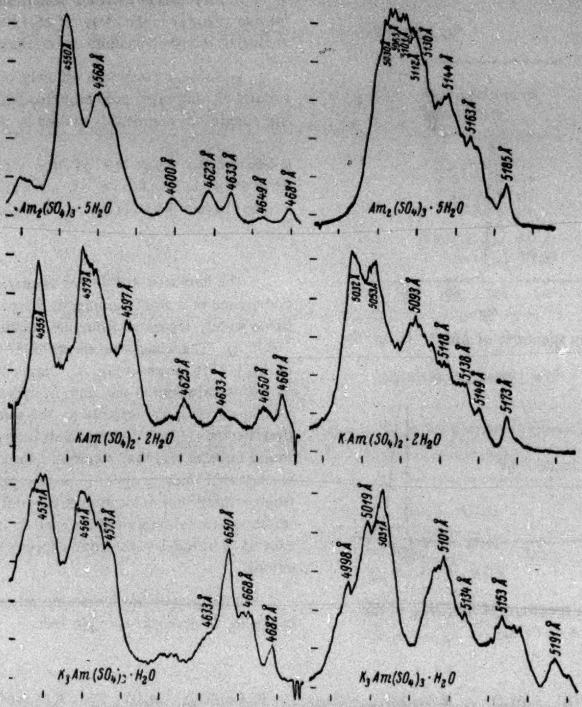

Fig. 5. Absorption spectra of americium compounds at 80°K.

A	A/mm
8000	196
7000	149
6000	87
5000	47
4500	28
4000	19

For plots in the 7000-8500 A region home-produced plates, "Infra-220 and 840," were used and also imported plates "Infrared 850, 950 and 1050." For plots in the 4000-5200 A region, Russian-produced isoorthochromatic contrast plates with a sensitivity of 45 GOST units were used. A 500-w incandescent lamp was used as the continuous spectrum source. Under these conditions the exposure times were from 10 seconds to 2 hours. The absorption spectra were recorded with a slit width of 0.025 mm. The spectra obtained were interpreted with the help of a reference spectrum (iron-arc spectrum) on an MIR-12 measuring microscope and were measured photometrically under standard conditions with an MF-4 recording microphotometer. Plotting of the absorption spectra was carried out at 300, 200 and 80°K (room temperature, the temperature of a mixture of excess solid carbon dioxide in acetone and the boiling point of nitrogen at atmospheric pressure). A $CuSO_4$ solution was used as heat-filter for plots at 300°K.

RESULTS OF MEASUREMENTS

From the absorption-spectrum plots of the materials studied in the region 4000-8500 A, it was discovered that the electronic bands of the hydrated Am^{+++} ion undergo specific peak separation in the 5030 and 8110 regions and in addition a group of "lines" was discovered that are not observed in Am^{+++} solutions or in the spectra of solid preparations of $Am(OH)_3$ (Fig. 4). Absorption bands were not found in the 5200-8000 A region. In the present work, attention was mainly concentrated on the peak separation in the intense electronic band at 5030 A and on the group of "lines" in the 4500 A region.

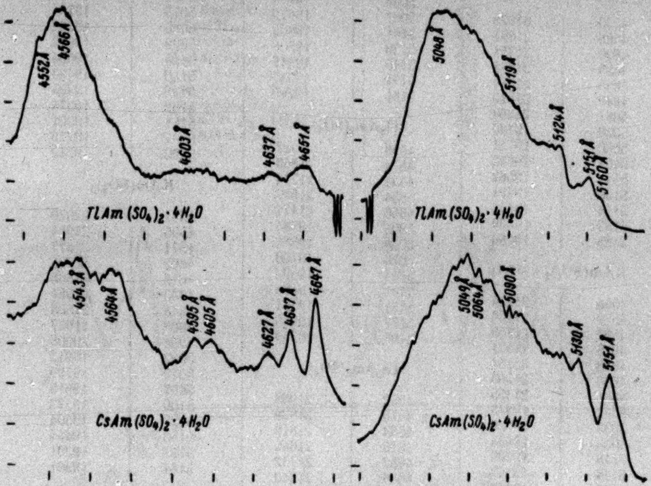

Fig. 6. Absorption spectra of americium compounds at 80°K.

Photomicrograms of the absorption spectra of the compounds indicated in the region 4500-5200 A at 80°K are shown in Figs. 5-8. Figure 9 shows photomicrograms of the absorption spectra of the double sulfate of americium and cesium precipitated at a ratio of $M_{Cs^+}/M_{Am^{+++}}$ of 129.1, at 300, 200 and 80°K.

As a secondary result a change in the absorption spectrum of the ordinary sulfate $Am_2(SO_4)_3 \cdot 5H_2O$ with time was noted, which is probably caused by disruption of the crystal lattice by α-irradiation from Am^{241}. Figure 10 shows an absorption-spectrum photomicrogram of the ordinary americium sulfate $Am_2(SO_4)_3 \cdot 5H_2O$ in the 4500 A region, recorded 15 days after preparation.

Figure 11 shows the peak separation in the split electronic band at 8110 A for $K_8Am_2(SO_4)_7$ at 80°K.

The wavelengths and wave numbers of the absorption-band maxima are shown in Table 5 for all the compounds examined, at 80°K in the 4500-5200 A region.

In Table 6 the magnitudes of the splitting of the 5030 A electronic bands at 80°K are quoted for the compounds studied.

DISCUSSION OF RESULTS

The data of Table 6 show that the absolute magnitude of the peak separation of the 5030 A electronic band of Am^{+++} is on the average considerably greater than that, for example, of neodymium or europium.

The increase in statistical interaction involved in the greater peak separation in the case of the actinides is possibly connected with an increase of the effective nuclear charge since the ionic radii of lanthanides and

TABLE 5

Wavelengths and Wave Numbers of the Absorption-Band Maxima for the Americium Compounds Studied, in the 4500-5200 A Region at 80°K

λ (Å)	ν (cm^{-1})
$Am_2(SO_4)_3 \cdot 5H_2O$	
4550	21978
4568	21891
4600	21751
4623	21631
4633	21584
4649	21510
4681	21363
5030	19880
5060	19741
5101	19602
5112	19562
5130	19491
5144	19440
5163	19369
5185	19286
$KAm(SO_4)_2 \cdot 2H_2O$	
4555	21954
4579	21836
4597	21753
4625	21621
4633	21584
4650	21505
4661	21455
5032	19873
5053	19720
5093	19634
5118	19536
5138	19463
5149	19419
5173	19331
$K_3Am(SO_4)_3 \cdot H_2O$	
4531	22070
4561	21925
4573	21867
4633	21584
4650	21505
4668	21422
4682	21358
4998	20008
5019	19924
5031	19879
5101	19602
5134	19478
5153	19406
5191	19264
$K_8Am_2(SO_4)_7$	
4556	21929
4568	21891
4649	21510
4665	21436
4995	20018
5033	19867
5066	197 9
5081	19679
5101	19602
5126	19508
5149	19419
5171	19337
5181	19299
$Tl_8Am_2(SO_4)_7$	
4558	21937
4574	21863
4592	21774
4634	21577
4656	21477
5004	19984
5028	19888
5076	19700
5104	19592
5131	19489
5151	19414
5177	19316
5190	19269
$Cs_8Am_2(SO_4)_7$	
4552	21968
4579	21839
4583	21818
4619	21649
4652	21732
4686	21340
4707	21245
4972	20112
4985	20060
5028	19888
5064	19747
5091	19642
5099	19611
5131	19489
5162	19372
5188	19275
5198	19238
$Am_2(SO_4)_3$	
4519	22129
4529	22080
4541	22021
4559	21935
4578	21844
4595	21763
4608	21701
4630	21598
4648	21515
4658	21466
4684	21347
4692	21311
5024	19904
5032	19873
5051	19798
5075	19704
5086	19662
5099	19612
5114	19554
5130	19493
5149	19421
5162	19374
5181	19301
5187	19279
5195	19249
$KAm(SO_4)_2$	
4531	22070
4555	21954
4571	21877
4602	21729
4615	21668
4633	21584
4648	21538
4668	21637
4998	20008
5022	19912
5079	19709
5097	19619
5109	19573
5127	19504
5143	19444
5157	19391
5181	19301
$TlAm(SO_4)_2 \cdot 4H_2O$	
4552	21966
4566	21901
4603	21724
4637	21563
4651	21501
5048	19810
5119	19535
5124	19517
5151	19418
5160	19380
$CsAm(SO_4)_2 \cdot 4H_2O$	
4543	22011
4564	21910
4595	21763
4605	21715
4627	21610
4637	21565
4647	21732
5049	19805
5064	19747
5090	19646
5130	19493
5151	19418

TABLE 6

Maximum Peak Separation in the Split Bands at 5030 A for Am^{+++} at 80°K in Crystals of the Compounds Studied (measured between the extremes of the maxima)

Compound	Peak separation of Am^{+++} band at 5030 A (cm^{-1})
$Am_2(SO_4)_3 \cdot 5H_2O$	594
$Am_2(SO_4)_3$	655
$KAm(SO_4)_2 \cdot 2H_2O$	542
$KAm(SO_4)_2$	707
$K_3Am(SO_4)_3 \cdot H_2O$	744
$K_8Am_2(SO_4)_7$	719
$TlAm(SO_4)_2 \cdot 4H_2O$	430
$Tl_8Am_2(SO_4)_7$	715
$CsAm(SO_4)_2 \cdot 4H_2O$	387
$Cs_8Am_2(SO_4)_7$	843

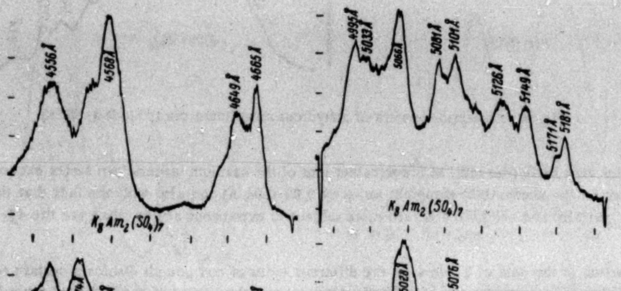

Fig. 7. Absorption spectra of americium compounds at 80°K.

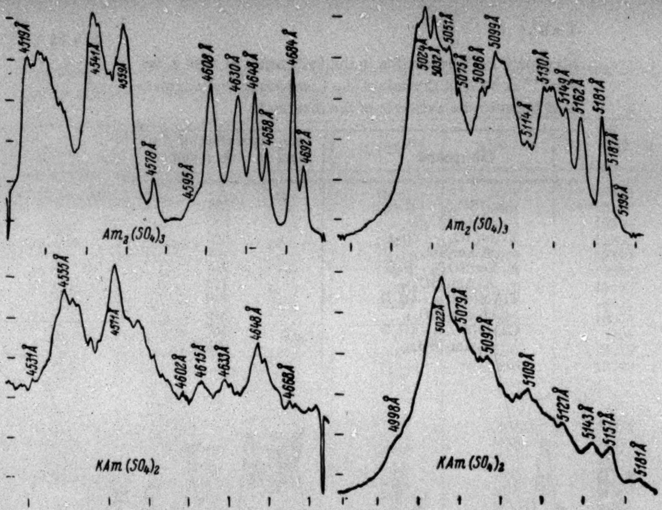

Fig. 8. Absorption spectra of anhydrous americium compounds at 80°K.

actinides differ very little (the radii of the trivalent ions of the uranium-americium series exceed the corresponding values for the neodymium-europium series by 0.03-0.04 A) and also with the fact that the 5*f*-electrons of actinides, spatially and energetically, are more subject to extraneous action than are the 4*f*-electrons of lanthanides.

Comparison of the data of Table 6 for the different series of compounds discloses certain relationships. The maximum peak separation in the split bands increases on dehydration of the hydrated crystals, probably as a result of the removal of water from the near neighborhood of the absorbing ion and strengthening of the field of the SO_4^{--} groups.

The increase in the total peak separation of the 5030 A band in the $R_8Am_2(SO_4)_7$ series of compounds from potassium and thallium to cesium might be connected with the increasing radius of the monovalent cation (K^+ 1.33; Tl^+ 1.44; Cs^+ 1.67 A) which suggests a maximal interaction (statistical effect) in the case of $Cs_8Am_2(SO_4)_7$. However, as is seen from Fig. 7, the width of the "lines," which characterizes the dynamic effect of interaction of the ion with the lattice, increases toward the $K_8Am_2(SO_4)_7$ side. Possibly in this case a more complex form of interaction takes place leading on the one hand to greater screening of the ion and on the other to an increase in the field that splits, with the result that one of these effects increases at the same time as the other decreases.

The absorption bands of compounds of the composition $R_8Am_2(SO_4)_7$ in the crystalline form consists of four components each of which is subdivided into two. For the bands at 8110 A this secondary splitting is not observed because of the low "dispersing power" of the apparatus in this region. A similar peak separation of the band at 5030 A into four components, as has already been stated, was noted for some americium compounds [9, 11]. Such a band structure allows the assumption that of two energy levels between which transfer takes place, one splits into two and the other into four sub-levels. As a result of transitions between these components, eight separate frequencies are observed.

From the increase in interaction with the environment observed in actinides, as exemplified by americium, the appearance of more intense electronic-vibrational "lines" in these cases would be expected.

In the study of the absorption spectra of americium compounds in the crystalline form, rather intense groups of lines, displaced toward the shortwave side of the electronic band of the order of magnitude of 1500-2000 cm^{-1},

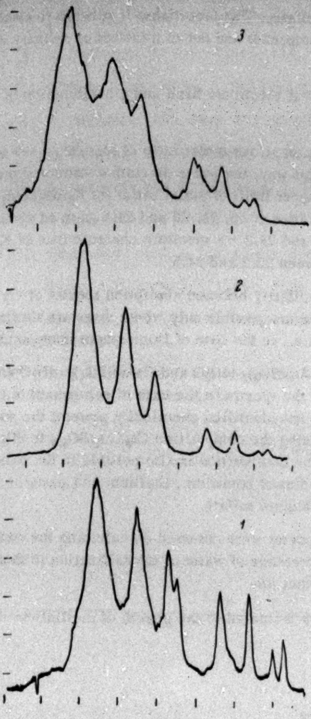

Fig. 9. Peak separation of the Am^{+++} band at 5030 A for $Cs_3Am_2(SO_4)_7$ at various temperatures (°K): 1) 80°; 2) 200°; 3) 300°.

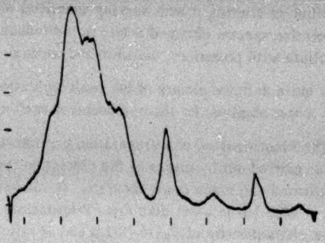

Fig. 10. Absorption spectrum of $Am_2(SO_4)_3 \cdot 5H_2O$ at 80°K in the 4500-A region 15 days after preparation.

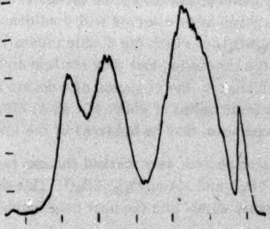

Fig. 11. Peak separation of the Am^{+++} band at 8110 A for $K_3Am_2(SO_4)_7$ at 80°K.

were observed. These lines are most sensitive to changes in composition of the compounds and they repeat in part the structure of the electronic band. It can be surmised that these lines have an electronic-vibrational origin. This is confirmed also by the fact that in the absorption spectrum of the Am^{+++} ion in solution and in crystals of $Am(OH)_3$ (Fig. 4) this group of lines is absent, because the interaction in these cases is evidently small.

Calculation has shown that the differences between the frequencies of these lines and the frequency of the maximum of the 5030 A electronic band do not coincide with the frequencies of the natural vibration of the sulfate ion (990, 1125 and 1340 cm^{-1}) and the water molecule (1640 cm^{-1}), known from Raman spectra data. For example, the following constant differences were found for compounds of the $R_3Am_2(SO_4)_7$ series:

$K_3Am_2(SO_4)_7$	$\Delta\gamma_1$	2021, 2047	(mean 2034 cm^{-1})
	$\Delta\gamma_2$	1502, 1571	(mean 1536 »
$Tl_3Am_2(SO_4)_7$	$\Delta\gamma_1$	2049, 2027	(mean 2038 »
	$\Delta\gamma_2$	1589, 1593	(mean 1591 »
$Cs_3Am_2(SO_4)_7$	$\Delta\gamma_1$	2042, 2080	(mean 2061 »
	$\Delta\gamma_2$	1749, 1761	(mean 1755 »
	$\Delta\gamma_3$	1452, 1498	(mean 1475 »

The noncoincidence of the differences cited with the natural frequencies of the neighboring anions and water molecules is evidently connected with the more complex nature of the americium ion with the lattice, as has already been stated above.

The chemical individuality of all the compounds studied was proved conclusively in the process of plotting the absorption spectra. As stated above, no change was observed in the nature of the absorption spectra of a preparation on diluting it with varying quantities of potassium sulfate. This fact makes it possible to assert that the absorption spectra obtained relate to individual chemical compounds and not to mixtures of ordinary americium sulfate with potassium, thallium and cesium sulfates.

A quite definite picture of the peak separation of the 5030 A electronic band and a combination of lines at 4500 A was obtained for the compound of each composition.

The identification of a preparation precipitated from solution at one molar ratio of $M_{R^+}/M_{Am^{+++}}$ or another, was carried out by means of the absorption spectrum; in this way, the phase diagram constructed previously was confirmed and made more accurate. It was found that the upper limit of molar ratios for $K_3Am(SO_4)_3 \cdot H_2O$ lies not at 37.9 but is lower than this. Preparations obtained at ratios of 36, 31, 26 and 24.5 gave an absorption spectrum characteristic of $K_8Am_2(SO_4)_7$ and at ratios of 15, 16.8 and 23.3 – a spectrum characteristic of $K_3Am(SO_4)_3 \cdot H_2O$. A new limit was established as a result of this, lying between 23.3 and 24.5.

There are statements in the literature to the effect that similarity between absorption spectra of crystals bears witness to their isomorphism [10]. Actually, similar spectra are possible only where there are similar crystalline fields which can occur in lattices of the same structure, i.e., in the case of isomorphous compounds.

Comparison of the absorption spectra of the compounds $TlAm(SO_4)_2 \cdot 4H_2O$ and $CsAm(SO_4)_2 \cdot 4H_2O$ enables their isomorphism to be assumed with confidence. The shape of the spectra in the case of compounds of the series $R_8Am_2(SO_4)_7$, of which the double sulfate with cesium was not identified chemically, presents the possibility of drawing the conclusion that they are isomorphous and of assigning the composition $Cs_8Am_2(SO_4)_7$ to this compound. Furthermore, the existence of a double sulfate of the same composition is also possible in the case of rubidium, the ionic radius of which is 1.48 A, close to the ionic radius of potassium, thallium and cesium; however, its preparation may be hindered by the low solubility of rubidium sulfate.

As was expected, very marked changes in the absorption spectra were observed on calcining the compounds $Am_2(SO_4)_3 \cdot 5H_2O$ and $KAm(SO_4)_2 \cdot 2H_2O$. This demonstrates the presence of water of crystallization in them, which evidently enters into the near neighborhood of the americium ion.

The broadening of the lines with temperature rise on Fig. 9 is related to the growth of oscillations in the crystal lattice.

SUMMARY

1. A number of americium compounds have been identified.

2. Phase diagrams have been drawn for the system $R_2SO_4-Am_2(SO_4)_3-H_2O$ (R = K, Tl or Rb).

3. The peak separation of the electronic band of Am^{+++} at 5030 A, in crystals of the compounds studied, has been examined.

4. A group of electronic-vibrational "lines" in the 4500 A region, that are not observed in solutions and are very sensitive to changes in composition of the compound, have been identified.

5. The effect of temperature and the presence of water of crystallization on the nature of the peak separation of the electronic band of Am^{+++} at 5030 A and on the combination of electronic-vibrational "lines" in the 4500 A region, has been examined.

6. The electrons of the 5*f*-shell interact more strongly with the field of the crystal lattice than do the electrons of the 4*f*-shell. This phenomenon could be used successfully in studying the interior structure of crystals.

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HYDROGEN EXCHANGE IN PHENOLS,
ITS ETHERS AND AROMATIC AMINES WITH LIQUID DBr

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The basic mechanism of deutero-exchange in aromatic hydrocarbons dissolved in liquid DBr has been established earlier [1, 2]. In this communication, results are reported from a study of hydrogen exchange with liquid DBr in aromatic compounds with substituents containing a hydrogen or nitrogen atom.*

The free electron pairs of the hydrogen or nitrogen atom of the substituent interact with the π-electrons of the aromatic ring as a result of which the electron density of the ortho and para atoms of the hydrocarbon is increased (π-conjugation, p-effect, see [4]). The addition of a proton (deuteron) to the electron pair of the nitrogen or hydrogen atom can bring about their transition to the four- or three-valent positively charged ions, respectively. These characteristics of the compounds mentioned determine the specific nature of their deutero-exchange with acids.

Hydrogen exchange in the compounds in which we are interested (with the exception of $C_6H_5OC_6H_5$) has been studied by a number of authors, but under conditions differing from ours. Small and Wolfenden [5] found that on heating phenol with D_2O at 100°, slow exchange of hydrogen in the ring takes place. Acids accelerate the exchange considerably. Ingold and co-workers [6] and Koizumi [7] showed that the exchange is of the electrophilic substitution type. The ortho and para hydrogen atoms take part in the exchange [8]. These same hydrogen atoms rapidly undergo exchange with gaseous DCl [9]. A.J. Brodskii, G.P. Miklukhin and their collaborators [10] studied the bimolecular reaction between hydroxy groups and the phenolic nucleus.

Deutero-exchange in anisole proceeds slowly with aqueous DCl but more rapidly with D_2SO_4 [6] and with glacial acetic acid (on catalysis with sulfuric acid) [11]. Exchange of three H atoms of the nucleus was achieved. Exchange of the ortho and para H atoms of the dimethylamine and aniline nuclei with aqueous DCl and D_2SO_4 proceeds more rapidly than is the case with phenol [6, 8].

Kharasch and Brown [12] found that the ortho and para H atoms of triphenylamine, diphenylamine and dimethylaniline exchange with C_2H_5OD on catalysis with D_2SO_4 at 100° for 100 hours.

EXPERIMENTAL

The apparatus for the preparation of liquid DBr and the method of carrying out deutero-exchange experiments has been described previously [13]. The exchange experiments were carried out usually at 20-25°. The number of hydrogen atoms "n" in aromatic compounds that are exchanged for deuterium, with concentrations of deuterium in HBr of less than 5 atoms %, was calculated according to Equation (10) (see [14]), and with concentrations > 80 atoms % — according to the equation $n = c_W N / c_S^0$ (1), where: c is the concentration of D in atoms % in the water of combustion of the materials and c_S^0 — in the hydrogen bromide, and N is the number of hydrogen atoms in the compound. Experiments on the reverse exchange were worked out according to Equation (11) (see [14]). c was determined by means of a spot method with an accuracy of up to 0.02-0.05 atoms %. In the case of high D concentrations the water from the combustion of the compounds was diluted by weight with water of normal isotopic composition. All the compounds studied were carefully purified and dried before carrying out the experiments. The weight of substance taken was usually 0.2-1.0 g and of solvent, 15-20 g.

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*Results of papers presented at the All-Union Conference on the Use of Isotopes [3]. The investigation of phenol and its ethers was part of the dissertation of A.V. Vedeneev Karpov (Phys.-Chem. Inst. (1955)).

Compounds. Phenol, "Pure for Analysis," was twice redistilled in vacuo in a current of dry nitrogen. The second distillation was carried out over anhydrous $CuSO_4$; m.p. 40.5-41°. Anisole, "pure," was fractionated in vacuo and dried over metallic sodium; b.p. 153.5°, $n^{20}D$ 1.5170. Dimethylaniline was steam-distilled, solidified by cooling, dried over metallic sodium and redistilled in vacuo, b.p. 192.5°, $n^{20}D$ 1.5583. Diphenylamine and triphenylamine were distilled in vacuo. Their melting points were 53.5 and 125.5°, respectively.

All the compounds are readily soluble in DBr, form colorless solutions and can be isolated unchanged from solution. The latter was shown by determination of the constants after exchange experiments. The phenol solution after 24 hours acquired a crimson, then violet, color. The anisole solution also behaved in the same way after 17 hours. On prolonging the experiments with phenol the quantity isolated was reduced. In experiments lasting more than 150 hours phenol could not be isolated. Anisole was even less stable. After 17 hours the anisole had been converted to phenol. The reaction evidently proceeds according to the equation $C_6H_5OCH_3 + HBr \rightarrow$ $\rightarrow C_6H_5OH + CH_3Br$. Phenol was identified by conversion to tribromophenol.

In order to terminate the deutero-exchange reaction the sealed glass tubes were plunged into liquid air. After this the DBr was evaporated off. The residue was extracted with ether. In the cases of dimethylamine and diphenylamine, which form the corresponding hydrobromides, aqueous alkali was added beforehand. The ethereal extracts were next dried over potassium carbonate (phenol, diphenylamine, dimethylaniline) and the ether was distilled off. In experiments with diphenylamine, in order to liberate deuterium in the NH group, the ethereal extract was extracted several times with water of the normal isotopic composition. After evaporation of the ether the materials were twice redistilled in vacuo (anisole, diphenyl ether and dimethylaniline over metallic sodium). After this treatment the constants of the materials showed no further change.

Already the first experiments with phenol, anisole, diphenyl ether and triphenylamine showed that hydrogen exchange with DBr proceeds very rapidly. Hence the exchange reaction equilibrium could be set up during the time of evaporation of the DBr, i.e., at a temperature of approximately −60° [14]. The values of the distribution coefficients which are necessary for the calculation of the number of hydrogen atoms exchanged, according to Equation (10) (see [14]), are known only approximately ($a \sim 5$) [15]. Consequently, the exchange experiments with C_6H_5OH, $C_6H_5OCH_3$, $(C_6H_5)_2O$ and $(C_6H_5)_3N$ had to be conducted with DBr containing 80-100 atoms % of D. In these circumstances n could be calculated approximately by Equation (1).

In the tables given below the following designations are used: T is the duration of experiment; t° is the temperature; m_C is the number of moles of compound; m_s is the number of moles of solvent; m_{AlBr_3} is the number of moles of $AlBr_3$ catalyst; c_s^0 is the concentration of deuterium in the solvent at the beginning of the experiment, in atoms %; c_W is the concentration of dueterium in the water of combustion of the compound at the end of the experiment; n is the number of atoms of deuterium (protium) exchanged; k is the rate constant of the hydrogen-exchange reaction, calculated according to the first-order reaction equation.

Hydrogen exchange in phenol (Table 1). Four of the hydrogen atoms in phenol are exchanged for deuterium very rapidly. One of these is that of the hydroxyl group and three deuterium atoms become attached to the ortho and para positions of the nucleus. This was verified by two methods. First the phenol after deuterization was brominated to 2,4,6-tribromophenol and the deuterium was removed from the hydroxyl group by washing with water of the normal isotopic composition. The water obtained from combustion of the tribromophenol was almost free of deuterium. Second, by heating phenol with heavy water in the presence of alkali, 2,4,6-trideuterophenol [6] was obtained. The reverse exchange of these materials with HBr was then carried out.

As is seen from Table 2, only a small quantity of deuterium [$c_{W(calc)}$] remained in the phenol after this, the amount of deuterium corresponding to the ratio of the compound and solvent allowing for the coefficient of distribution of deuterium a between the bonds C−H and H−Br.*

Hydrogen exchange in anisole (Table 1). The three hydrogen atoms in the ortho and para positions in the nucleus exchange very rapidly. This was shown in the following way. 2,4,6-Trideuterophenol, prepared as described above, was methylated with dimethylsulfate. The 2,4,6-trideuteroanisole was then treated with liquid HBr. The results (Table 2) indicate that the ortho and para atoms undergo exchange.

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*As is seen from Table 1, in all experiments with phenol for exchange of H in the nucleus a value of $n < 3$ was obtained. The reason for this is not clear to us.

TABLE 1

Isotopic Hydrogen Exchange in Phenol, Anisole and Diphenyl Ether

Expt. No.	T	$t°$	c_S^0	c_W	n	$\frac{m_{AlBr_3}}{m_W}$
			Phenol			
1	10 min	Room	91.0	53.0	3.5	
2	30 »	25	91.0	55.1	3.6	
3	3 hours	25	91.0	53.1	3.5	
4	27 »	Room	91.0	55.0	3.6	
5	72 »	»	88.8	37.3	2.5*	
6	150 »	»	88.8	39.0	2.6*	
			Anisole			
7	5 min	Room	93.7	32.9	2.8	
8	10 »	»	90.9	35.1	3.1	
9	30 »	25	90.9	33.8	3.0	
10	3 hours	25	93.7	33.9	2.9	
11	6 »	25	93.7	31.2	2.7	
12	5 min	Room	83.5	42.0	4.0	0.9
13	30 »	25	93.7	43.6	3.7	0.8
			Diphenyl ether			
14	10 »	Room	90.9	55.0	6.0	
15	3 hours	25	90.9	55.0	6.0	
16	24 »	Room	88.8	54.3	6.1	
17	26 »	»	90.9	55.9	6.1	
18	150 »	»	88.8	51.8	5.8	
19	313 »	»	93.7	57.3	6.1	
20	1 »	25	100	83.4	8.3	1.3
21	1 »	25	100	90.9	9.0	0.5
22	3 »	25	100	95.4	9.5	1.0

---

*Deuterium was washed out from the hydroxyl with water of normal isotopic composition.

Experiments were set up to examine the effect of addition of $AlBr_3$ on the rate of hydrogen exchange. As is known, $AlBr_3$ markedly increases the acidity of solutions in liquid DBr. As is seen from the data of Table 1 (experiments 12 and 13), the presence of $AlBr_3$ brings about additional exchange beyond three atoms (evidently, in the meta position). Unfortunately, after only one hour in the presence of $AlBr_3$ anisole undergoes irreversible changes and its isolation is impossible (in an analogous experiment with phenol the latter could not be isolated after being acted upon by $AlBr_3$ for only five minutes).

Hydrogen exchange in diphenyl ether (Table 1). Six hydrogen atoms exchange very rapidly. It is natural to assume that these are the ortho and para hydrogen atoms. In order to verify this assumption, decadeuterodiphenyl ether was prepared by exhaustive deuterization of diphenyl ether in a solution of potassium amide in ND_3. On carrying out the reverse exchange of decadeuterodiphenyl ether with liquid HBr (Table 2) in ether, only an amount of deuterium corresponding to four deuterium atoms were left, remaining in the meta positions in the nucleus. It was not possible to exchange more than six atoms with liquid DBr even in experiments lasting 300 hours. However, increasing the acidity of the solution by addition of $AlBr_3$ resulted in all ten hydrogen atoms being exchanged in only three hours. Therefore, the meta atoms also took part in the exchange.

Hydrogen exchange in triphenylamine, diphenylamine and dimethylaniline (Table 3). In triphenylamine nine hydrogen atoms undergo exchange in five minutes. Further exchange was not observed even after 200 hours. On addition of $AlBr_3$ the rate of hydrogen exchange is markedly reduced (Table 3, experiments 5-7). During five minutes, instead of nine hydrogen atoms, less than one is exchanged.

Hydrogen exchange proceeds considerably more slowly in diphenylamine than in triphenylamine. The exchange of six hydrogen atoms could be effected only after 1000 hours. The addition of $AlBr_3$ gave no marked effect on the rate of hydrogen exchange (experiment 9).

TABLE 2

Experiments on Reverse Exchange With Liquid HBr at 25°

Expt. No.	τ (min)	$\frac{m_s}{m_w}$	c_w^0	c_w	$\overset{\bullet}{c}_w$ (calc)
		2,4,6-D-phenol			
1	5	50	3.23	1.04	0.7
2	5	48	3.23	1.22	0.8
3	30	32	3.23	1.14	0.9
		2,4,6-D-anisole			
4	5	80	2.27	0.55	0.55
5	5	59	2.27	0.65	0.63
6	30	38	2.27	0.77	0.77
		Decadeuterophenyl ether			
7	10	150	8.84	4.32	4.64
8	10	230	8.84	4.15	4.24

---

*c_w(calc) is the calculated concentration of deuterium in the water from the combustion of the substances after the experiment. The number of exchangeable atoms for phenol and anisole was taken as 3, for diphenyl ether as 6, and the distribution coefficient a, as 5.

Hydrogen exchange in dimethylaniline was practically absent even in experiments lasting more than 1100 hours. The presence of $AlBr_3$ had no effect on the rate of deutero-exchange (experiment 17).

DISCUSSION OF RESULTS

In phenol and its ethers, deutero-exchange proceeds in a similar manner. The ortho and para hydrogen atoms of the nucleus exchange very rapidly but further exchange was not observed even over a long period of time. Such a rapid exchange of the nuclear hydrogen atoms is evidently explained by the increased electron density in the ortho and para positions as a result of the π-conjugation p-effect. According to A.N. Nesmeianov's terminology [4], transference of the reaction center from the hydrogen atom to a ring carbon atom in the ortho or para position takes place. How strongly the exchange reaction is accelerated as a result of the π-conjugation p-effect is seen by comparison of the rates of hydrogen exchange of phenol, anisole and diphenyl ether with the corresponding hydrocarbons. In benzene the exchange proceeds extremely slowly ($k_{20°} = 5 \cdot 10^{-8}\ \mathrm{sec}^{-}$ [1]); in toluene and diphenyl, exchange of the para and ortho atoms proceeds much more rapidly ($k_{25°} = 10^{-4}\text{-}10^{-5}\ \mathrm{sec}^{-1}$) [1, 2].

How much the rate of hydrogen exchange depends on the acidity of the deuterizing agent is seen from the fact that on heating phenol for 400 hours at 100° only two nuclear hydrogen atoms are exchanged [5] and anisole does not take part in an exchange reaction with heavy water.

Hydrogen exchange in aromatic amines with liquid DBr, in contrast to phenol and its ethers, proceeds quite differently. In triphenylamine nine atoms exchange extremely rapidly. While in dimethylaniline deutero-exchange did not occur even in experiments carried on for more than 1100 hours. Diphenylamine, in which six hydrogen-exchange atoms are exchanged very slowly, occupies an intermediate position.

According to Karasch [12] all three of the above-mentioned amines exchange the ortho and para nuclear hydrogen atoms in C_2H_5OD on catalysis with D_2SO_4 (at 100° and an acid concentration of 0.6 N).

The different behavior of the aromatic amines in hydrogen exchange must be ascribed to their dissimilar basicities. As is known, the basicity falls in the order: dimethylaniline > diphenylamine > triphenylamine. Whereas dimethylamine forms a very stable salt with DBr, triphenylamine does not give a salt with DBr. Diphenylamine is intermediate between the two.

TABLE 3

Isotopic Exchange in Triphenylamine, Diphenylamine and Dimethylaniline

Expt. No.	T	$t°$	$\frac{m_S}{m_W}$	$\frac{m_{AlBr_3}}{m_W}$	c_S^0	c_W	n
				Triphenylamine			
1	5 min	Room			83.5	48.8	8.8
2	2 hours	25			88.8	51.2	8.7
3	2 »	25			83.9	47.5	8.5
4	200 »	Room			93.7	52.5	8.4
5	5 min	»		1.2	93.7	3.1	0.5
6	5 »	»		1.0	~100	2.6	0.4
7	5 »	»		0.4	~100	27.4	4.1
				Diphenylamine			
8	1 hours	25	100		5.4	0.2	0.1
9	1 »	25	140	0.5	5.4	0.2	0.1
10	2 »	25	90		88.8	2.6	0.3
11	24 »	Room	140		9.0	2.0	1.1
12	97 »	»	140		9.0	6.6	3.9
13	120 »	»	74		4.4	4.0	5.2
14	696 »	»	59		4.4	4.7	5.6
15	1152 »	»	110		4.4	5.3	6.0
				Dimethylaniline			
16	1 hours	25	50		5.4	0.1	~0
17	1 »	25	51	0.3	5.4	0.1	~0
18	696 »	Room	91		4.4	0.1	~0
19	1152 »	»	97		4.4	0.1	~0
20	1152 »	»	63		4.4	0.02	~0

On dissolving dimethylaniline in liquid DBr a deuteron adds on to the free electron pair of the nitrogen atom which becomes tetravalent.

The conjugation of the p-electrons with the π-electrons of the nucleus is disrupted and the ortho and para carbon atoms cease to be negatively charged. Consequently, a deuteron cannot add on to them, which is the necessary condition for hydrogen exchange in an acid medium. The failure of dimethylaniline to undergo exchange is possibly explained also by the fact that this substance forms a positively charged ion, the addition of a deuteron to which is hindered.

In triphenylamine, where no salt is formed, on the other hand the π-conjugation p-effect is fully manifested and exchange with the strongly acidic DBr takes place rapidly. Although diphenylamine forms a salt with the acid the π-conjugation p-effect is nevertheless appreciable, inasmuch as slow deutero-exchange of the ortho and para hydrogen atoms takes place. This result confirms that acid-base interaction does not certainly lead to complete transfer of a proton (deuteron) of the acid to the base [16].

It was of interest to examine whether it is possible, by still further increasing the acidity of the solution, to eliminate the action of the π-conjugation p-effect,as occurs in the case of dimethylaniline. It was found that $AlBr_3$ markedly retards the rate of hydrogen exchange in triphenylamine. On addition of the stoichiometric quantity of $AlBr_3$ to triphenylamine,in five minutes less than one hydrogen atom undergoes exchange instead of nine. Evidently, addition of $AlBr_3$ increases the acidity of the medium to such an extent that a deuteron is added on to the free pair of p-electrons of the nitrogen atom with formation of the salt $(C_6H_5)_3ND^+AlBr_4^-$. It is possible,also, that $AlBr_3$ coordinates with the nitrogen atom. A.V. Topchiev [17] found that the addition of BF_3 to the nitrogen atom of aniline in nitration of the latter, sharply reduces the yield of the ortho and para isomers. As is seen from the data of Table 3 (experiment 7), if $AlBr_3$ is added in a quantity less than equimolecular the rate of exchange is higher. This result is quite understandable inasmuch as only a part of the triphenylamine molecule forms a salt (or coordinates with $AlBr_3$).

Addition of $AlBr_3$ to diphenyl ether and anisole not only does not decrease, but on the other hand increases the rate of hydrogen exchange. This indicates that neither formation of the corresponding oxonium salt nor coordination of $AlBr_3$ with a hydrogen atom takes place.

The different behavior with respect to hydrogen exchange of phenol and its ethers on the one hand and aromatic amines on the other is explained by the dissimilar coordinating power and different affinity for a proton of the hydrogen and nitrogen atoms. It is sufficient to recall only that in aqueous solution phenol is a weak acid and aniline reacts as a weak base.

SUMMARY

1. Hydrogen exchange in phenol and its ethers ($C_6H_5OCH_3$, $C_6H_5OC_6H_5$) and in aromatic amines ($C_6H_5N(CH_3)_2$, $(C_6H_5)_2NH$, $(C_6H_5)_3N$) with liquid DBr and also with DBr + $AlBr_3$ at 25° has been studied.

2. In all the compounds of the first group the ortho and para hydrogen atoms exchange instantaneously, but in the second group of compounds rapid exchange is observed only in $(C_6H_5)_3N$, whereas in $(C_6H_5)_2NH$ exchange of the atoms mentioned proceeds very slowly, and in $C_6H_5N(CH_3)_2$ it is not observed even after 1000 hours. $AlBr_3$ brings about exchange of the meta atoms in the phenyl ethers and retards the exchange reaction rate in $(C_6H_5)_3N$.

3. The specific nature of deutero-exchange in aromatic compounds with substituents containing hydrogen or nitrogen atoms is explained by the π-conjugation p-effect. The difference in behavior with respect to hydrogen exchange with liquid DBr and DBr + $AlBr_3$ of substances containing hydrogen and nitrogen is connected with their dissimilar affinities for a proton and the difference in coordinating power of the hydrogen and nitrogen atoms.

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HYDROGEN EXCHANGE OF PHENOL AND ITS ETHERS WITH SOLUTIONS OF POTASSAMIDE IN LIQUID DEUTEROAMMONIA

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In a previous communication [1] it was shown that the hydrogen-exchange capacity of phenol and its ethers and aromatic amines with liquid DBr is explained by the effect of p,π-conjugation and these reactions are affected by the different proton affinities and coordinating capacities of the oxygen and nitrogen atoms of the substituents in these compounds.

In this report we describe results obtained in studying the hydrogen exchange of phenol and its ethers with solutions of KND_2 in liquid ND_3. They supplement our ideas on the mutual effect of the atoms in molecules of the given substances and lead to certain conclusions on the mechanism of hydrogen exchange.*

EXPERIMENTAL

The procedure was described previously [2]. Particular attention was paid to drying the apparatus, the starting materials and the solvents since potassamide reacts readily with moisture. The operations connected with taking samples were either performed in a special "dry" box or in a stream of dry nitrogen. The samples of material were usually 0.2-0.5 g and of solvent, 3-5 g. At temperatures up to 40°, the experiments were performed in glass ampoules and at higher temperatures, in stainless-steel ampoules. The preparations of phenol, anisole and diphenyl ether were the same as in the work with liquid DBr [1]. n, the number of hydrogen atoms exchanged for deuterium, was calculated by the formula

$$n = \frac{c_W \cdot H}{\alpha\left[c_W^0 - \frac{c \cdot H \cdot H_0 \cdot m_W}{H_s \cdot n_t \cdot m_s}\right]},$$

where: c_W and c_s^0 are the D concentrations in at.% in water from combustion of the substance and the solvent before the experiment; α is the distribution coefficient of deuterium between the N−H and C−H bonds and equals 0.92 [3]; H is the number of hydrogen atoms in the substance; H_0 is the number of exchangeable hydrogen atoms in the substance; H_s is the number of exchangeable hydrogen atoms in the solvent; n_t is the number of hydrogen atoms in the substance, exchanged up to the given moment of time, calculated by the formula $n_t = \frac{c_W \cdot H}{\alpha c_s^0}$; m_W is the number of moles of substance and m_p the number of moles of solvent.

The rate constants of hydrogen exchange were calculated from a first-order equation.

Hydrogen exchange in phenol. In the first approximation, we neglected the ammonolysis of potassium phenolate, formed by reaction with KND_2, and considered that the solution of the phenol consumed an equivalent amount of amide. At the end of the deuterium-exchange experiment, the reaction mixture was poured into dilute HCl solution. The phenol was extracted with ether, the ether solution dried with baked Na_2SO_4 and the phenol vacuum distilled twice. After the experiments the phenol had m.p. 40.5-41°. The results of the experi-

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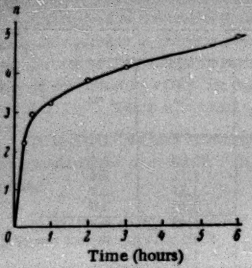
*The results were presented at the conference on the use of isotopes in April 1957. They are from the dissertation of A.V. Vedeneev [Karpov Phys. Chem. Inst. (1955)].



Hydrogen-exchange kinetics of anisole in a 0.03-N solution of KND_2 in ND_3 at 25°.

ments are shown by the data in Table 1. The symbols used in the tables are the same as in the previous communication [1]: c_{KND_2} is the concentration of potassamide in the solution (N) and c_W^1 the concentration of D in at. % in water from combustion of tribromophenol.

The fact that hydrogen exchange in the phenolate ion proceeds very slowly attracts attention. Heating for 200 hours at 120° was required to exchange all the hydrogen atoms. This is explained by the fact that the ring of the phenolate ion is negatively charged and the approach of the ND_2^- ion (a condition of exchange) is hindered. If the effect of p,π-conjugation played a determining role in the exchange of the phenolate ion with a solution of KND_2 in ND_3, then the first hydrogens to exchange should be those in the meta-positions, i.e., the positions with the lowest electron density. To test this hypothesis, experiments 5, 6 and 8 (Table 1) were stopped when, on a statistical average, about 1 hydrogen atom had exchanged. The phenolate was converted into phenol and the latter into 2,4,6-tribromophenol. If the meta H atoms were to be first to exchange, then the concentration (c_W^1) from combustion of the tribromophenol would be higher than that (c_W) from combustion of the phenol. If the ortho and para H atoms were to exchange, then $c_W^1 = 0$.

As the data in Table 1 show (last column), $c_W^1 < c_W$. This may be interpreted as meaning that all the H atoms in $C_6H_5O^-$ exchange with approximately the same probability. Evidently, under the action of a very strong base, the differences in "acidity" of the hydrogen atoms of the aromatic ring are leveled out, as usually occurs with acids that are dissolved in protophilic solvents [4].

A comparison of the rate of H-atom exchange in the phenolate ion and benzene showed that at $c_{KND_2} = 0.4$ N, $k_{50°} = 5 \cdot 10^{-6}$ and $8 \cdot 10^{-3}$, respectively (calculated data from [5]), i.e., the reaction of the phenolate ion is three orders slower.

TABLE 1

Hydrogen Exchange in Phenol: $c_{KND_2} = 1.19$ N; $c_S^0 = 9.10$ at. %

Expt. No.	τ (hrs)	t°	$\dot{c}_{KND_2}$	$\frac{m_S}{m_W}$	$\frac{m_{KND_2}}{m_W}$	c_W	n	c_W^1
1	1	25	0.20	33	0.19	0.12	0.1	
2	12	25	0.46	49	0.64	0.21	0.2	
3	6	50	0.37	43	0.27	0.60	0.4	
	16	~20						
4	8	50	0.20	44	0.24	0.90	0.6	
5	9	50	0.41	45	0.53	1.01	0.7	0.49
6	8	50	0.37	46	0.48	1.07	0.8	0.46
7	75	35	0.43	47	0.57	1.55	1.1	
8	19	50	0.40	45	0.51	2.04	1.5	1.03
	27	20						
9	221	100	0.53	54	0.42	5.90	4.3	
10	201	120	0.79	88	1.97	6.50	4.8	

Hydrogen exchange in anisole. A solution of anisole in ND_3 + KND_2 had a yellow-green color. To stop the exchange reaction, the reaction mixture was cooled to −70°. When the ammonia had been distilled away at low temperature, the anisole was vacuum distilled over anhydrous copper sulfate, which bound the ammonia residues. In experiments lasting more than a day, evaporation of the ammonia left a gelatinous mass, from which the anisole was extracted with absolute ether. After this treatment, the constants of the anisole remained unchanged. The results obtained are presented in Table 2. All the H atoms in anisole could be exchanged.

TABLE 2

Hydrogen Exchange in Anisole: $c_{KND_2} = 0.028$ N

Expt. No.	T	$t°$	$\frac{m_s}{m_W}$	$\frac{m_{KND_2}}{m_W}$	c_s^0	c_W	n
1	15 min	25	184	0.14	4.38	1.03	2.1
2	15 »	25	61	0.05	4.38	1.11	2.3
3	30 »	25	49	0.04	4.38	1.31	2.8
4	30 »	25	40	0.04	9.46	3.10	3.0
5	1 hours	25	40	0.03	4.38	1.48	3.2
6	1 »	25	47	0.04	4.38	1.53	3.2
7	2 »	25	48	0.04	4.38	1.77	3.8
8	3 »	25	41	0.03	4.38	1.87	4.1
9	3 »	25	43	0.03	4.38	1.95	4.1
10	6 »	25	44	0.03	4.38	2.33	4.9
11	6 »	25	85	0.06	4.38	2.42	5.0
12	22 »	~20	41	0.03	4.38	2.75	5.9
13	89 »	~20	40	0.03	9.46	6.55	7.0
14	144 »	~20	47	0.01	9.46	7.66	7.6

The extent of their nonequivalence is indicated by the kinetic curve (see the figure). To establish the sequence in which the H atoms exchange in anisole, preparations labeled in different positions were synthesized.

2,4,6-Trideuteroanisole was prepared by a dimethyl-sulfate methylation of 2,4,6-trideuterophenol, prepared by isotope exchange of hydrogen in phenol with a solution of alkali in D_2O [6].

Pentadeuteroanisole, $C_6D_5OCH_3$ was prepared by isotope exchange with DF.*

Then the number of D atoms left after treatment of these preparations with KNH_2 in NH_3 was determined. The results are presented in Table 3.

TABLE 3

Experiments on the Reverse Exchange With Deuterated Anisole Preparations at 25°

Expt. No.	c_s^0	Number of D atoms	c_{KNH_2}	T	$\frac{m_s}{m_W}$	c_W	Number of D atoms left	Number of D atoms replaced
				2,4,6-Trideuteroanisole				
1	2.27	2.7	0.03	5 min	60	0.87	1.0	1.7
2		3.0	0.10	5 »	51		1.0	2.0
3	2.27	2.7	0.04	30 »	66	0.77	1.0	1.7
4	2.27	2.7	0.04	30 »	50	0.77	1.0	1.7
5	2.27	2.7	0.03	30 »	63	0.74	1.0	1.7
6	2.27	2.7	0.04	1 hr	71	0.77	1.0	1.7
7	2.27	2.7	0.03	6 »	56	0.44	0.6	2.1
				2,3,4,5,6-Pentadeuteroanisole				
8	2.66	4.7	0.03	30 min	52	1.29	2.5	2.2
9	2.66	4.7	0.03	6 hr	60	0.28	0.6	4.1
10	2.66	4.7	0.03	6 »	58	0.26	0.5	4.2

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*Experiments on the exchange with HF and DF were performed together with Ia.M. Varshavskii, to whom we are grateful.

Comparison of the results shows that the ortho D atoms exchange very rapidly, then the meta atoms and finally the hydrogen in the para position. These data agree with the conclusions of Roberts, et al. [7]. By measuring the rate of D exchange in isomers of monodeuteroanisole with a solution of KNH_2 in NH_3 at −33.5°, they obtained the following values for the rate constants (sec^{-1}) for exchange of ortho, meta and para atoms: $9 \cdot 10^{-4}$, $1 \cdot 10^{-7}$, $1 \cdot 10^{-8}$. Deuterium exchange in monodeuterobenzene proceeds at a rate of $\sim 10^{-7}$ sec^{-1}.

To compare the rate of exchange of hydrogen in the methoxy group with that of the H atoms in the ring that are substituted most slowly – the para atoms – we used preparations of trideuteroanisole and 4-monodeuteroanisole.

Trideuteroanisole, $C_6H_5OCD_3$, was prepared by exhaustive exchange with a solution of KND_2 in ND_3 with subsequent treatment with HF.*

4-Monodeuteroanisole, $C_6H_4DOCH_3$, was prepared from 2,4,6-trideuteroanisole by two treatments (at room temperature for ten minutes) with a 0.03-N solution of KNH_2. Under these conditions only the ortho H atoms exchanged and the para atom was hardly involved.

The rate of exchange of the para H atom in the ring ($3 \cdot 10^{-4}$ sec^{-1}) was twice as great as in the methoxyl group ($\sim 1.4 \cdot 10^{-4}$ sec^{-1}) (Table 4). Comparison of the rate of exchange of the para H atom in anisole with that of the H atoms in benzene shows that at $c_{KND_2} = 0.27$ N, $k_{25°} = 3 \cdot 10^{-4}$ and $6 \cdot 10^{-4}$, respectively (recalculated data from [5]). Thus, the exchange of a hydrogen in benzene proceeds approximately twice as fast as in the para position of anisole. The methoxyl group exchanges approximately four times more slowly than H atoms in benzene.

TABLE 4

Kinetics of Reverse Exchange: $c_{KNH_2} = 0.27$ N, 25°

Expt. No.	c_W^0	τ (hours)	$\frac{m_s}{m_W}$	c_W	$k \cdot 10^{-4}$ (sec^{-1})
			$C_6H_5OCD_3$		
1	3.27	1.0	105	2.08	1.3
2	3.27	1.5	127	1.58	1.3
3	3.27	1.5	160	1.53	1.4
4	3.27	2.0	168	1.11	1.5
			4 - Monodeuteroanisole		
5	3.21	0.5	135	1.85	3.1
6	3.21	0,66	190	1.48	3.2
7	3.21	0.66	127	1.58	2.9
8	3.21	1.0	185	1.05	3.1
9	3.21	1.0	150	1.05	3.1
10	3.21	1.5	170	0.66	2.9

If we assume that the effect of conjugation plays the main role in the exchange of hydrogen in anisole with solutions of KND_2 in ND_3, then we would expect a completely different sequence of hydrogen exchange in the ring than that observed, namely, meta > para, ortho. The actual decrease in H-exchange rate in the anisole ring is in the order ortho > meta > para and compels us to assume that the determining effect in hydrogen exchange in anisole with solutions of $KND_2 + ND_3$ is the inductive effect of the oxygen atom.

In work from our laboratory, the strong analogy between deuterium-exchange reactions with nucleophilic reagents and metallation reactions has been stressed repeatedly [8, 9]. What is known about the metallation of anisole?

Wittig et al. [10] established that in the metallation of dimethylaniline, anisole and fluorobenzene with phenyllithium, only the ortho-H atoms were substituted and the rate of metallation increased in the order given. Wittig explained these results by the fact that the electronegativities of the heteroatoms attached to the ring (N, O and F) increased in the same order. Since the inductive effect is rapidly attenuated along a chain of carbon atoms, the ortho-H atoms will be protonized more readily than the other atoms. It is for just this reason that a metal replaces only the ortho atoms and the rate of metallation increases in the given order. Roberts [7] showed that the rule noted by Wittig was also observed in hydrogen exchange with solutions of potassamide in liquid ammonia in isomers of monodeuterofluorobenzene and deuteroanisole. The rate constants of the reverse exchange of D in o-, m- and p-monodeuterofluorobenzenes were equal to $4 \cdot 10^{-1}$, $4 \cdot 10^{-4}$ and $2 \cdot 10^{-6}$ sec^{-1}, respectively. Due to the high electronegativity of the fluorine atom in comparison with oxygen, in the case of fluorobenzene, the absolute value of the constant was higher than in the case of anisole.

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*It was established experimentally (together with Ia.M. Varshavskii and M.G. Lozhkina) that only the ring H atoms of anisole exchange with liquid DF and those of the methoxyl group are not involved. The experiments will be described later.

Of the results that we obtained, we should note particularly the fact that it was possible to exchange all eight H atoms in anisole, including those in the methoxyl group. This fact* was already established in 1950 [11]. Thus, the aromatic ring affects the lability of the H atoms in the C–H bonds, separated by an oxygen atom. This is also confirmed by experiments with methoxynaphthalene [14]. This phenomenon is even more widespread: the effect of the aromatic ring on an aliphatic bond is also transmitted by a nitrogen atom. This follows from the complete exchange of hydrogen in dimethylaniline and dimethylnaphthalene [11].

In connection with the above, it was also interesting to compare the exchange of hydrogen in toluene and anisole with solutions of $KND_2 + ND_3$. In contrast to anisole, the hydrogen atoms in the methyl group of toluene [12] exchanged considerably more rapidly (~250 times) than those in the ring. The acidity of the H atoms of the methyl group of toluene is sufficient for them to be substituted by cesium [13].

What is the reason for the exchange of hydrogen in the OCH_3 group of anisole? In analogy with the σ,π-conjugation effect (for example, in toluene), the effect of the ring on the mobility of the hydrogen atoms of the CH_3O group may be considered as a π,p,σ-conjugation effect. There is an indication of this in the review article by Wiles [14]. He notes that with such conjugation present, the C–O bond in the anisole molecule must be shortened; this is confirmed by x-ray data. In the opinion of the author, one should be rather careful in interpreting these data.

It is quite possible that in this case the determining role is played by an inductive displacement of the electrons at the oxygen atom, facilitating the protonization of H atoms in the methoxyl group. This hypothesis is supported by the results of experiments by Lauer and Day [15] on the exchange of deuterium, introduced chemically into the position para to the alkoxyl group in phenyl alkyl ethers. The solvent was glacial acetic acid and the catalyst, H_2SO_4. It was found that the rate of electrophilic replacement of the para-D atom in the aromatic ring increased in an order corresponding to the inductive effect of the alkyl group, namely: $CH_3(3.0) < C_2H_5(4.0) = C_3H_7(4.0) < \text{iso-}C_3H_7(7.5)$. The rate constants ($k \cdot 10^4$ sec^{-1}) are given in brackets.

We should note, however, that the peculiarities of hydrogen exchange in anisole with solutions of potassamide in liquid ammonia, cannot all be explained by the inductive effect of the hydrogen atom of the methoxyl group. For example, it is not clear why the H atoms of the ring exchange more rapidly than the H atoms of the methoxyl group in this case. Since the inductive effect is rapidly attenuated along a chain of carbon atoms, then the H atoms in the methoxyl group should exchange more rapidly than the meta atoms and much more rapidly than the para-H atoms. Evidently, the mutual effect of the atoms in the anisole molecule has its peculiarities, which require further study and cannot be interpreted from the generally accepted point of view at the moment.

Hydrogen exchange in diphenyl ether. $(C_6H_5)_2O$ is readily soluble in ND_3. In the presence of KND_2, the solutions acquired a yellow color. The substance was isolated after the experiment, as with anisole, and distilled in vacuum over sodium. The constants were unchanged after the experiment. The results of the exchange experiments are shown by the data in Table 5.

After only 15 minutes, the hydrogen exchange was close to complete. Under the same conditions, benzene

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*We should note that in his work [7] Roberts mentioned neither this fact nor all the work on hydrogen exchange in liquid ammonia, performed in the Isotope Reaction Laboratory of the Karpov Institute from 1947 onward. Roberts implied that the study of hydrogen exchange in solutions of potassamide in liquid ammonia originated in the USA in 1954.

TABLE 5

Hydrogen Exchange in Diphenyl Ether (25°)

Expt. No.	T	c_{KND_2}	$\frac{m_S}{m_W}$	$\frac{m_{KND_2}}{m_W}$	c_S^0	c_W	n
1	15 min	0.028	62	0.05	4.38	3.07	8.1
2	15 »	0.046	190	0.25	5.34	4.42	9.1
3	20 »	0.049	63	0.09	5.36	4.03	8.7
4	1 hours	0.028	70	0.06	4.38	3.50	9.2
5	1 »	0.046	83	0.11	5.34	4.86	10.2

exchanged less than a third of its H atoms (1.8 out of 6), anisole exchanged only the two most labile ortho-H atoms in the ring and diphenyl [12] exchanged about 2 H atoms. Consequently, the exchange of hydrogen in diphenyl ether proceeds much more rapidly than that in benzene, anisole and diphenyl. If hydrogen exchange in $(C_6H_5)_2O$ with ammoniacal alkali, as in the case of exchange with acid DBr [1], depended on p,π-conjugation, then one would expect the hydrogen exchange to be slower than in benzene. Actually, the exchange occurs more rapidly, regardless of whether an acid or a base participates in the reaction.

Diphenyl ether differs from anisole in that the position of the methyl group, which lacks π-electrons, is occupied by a phenyl group. The $(C_6H_5)_2O$ molecule has a polarizability ($20.8 \cdot 10^{-24}$ cm^3) greater than the anisole molecule ($13.1 \cdot 10^{-24}$ cm^3). Apparently, this plays a determining role in hydrogen exchange with a base.

DISCUSSION OF RESULTS

Data obtained by studying hydrogen exchange in oxygen- and nitrogen-containing aromatic compounds with acidic [1] and basic solvents, leads to certain conclusions on the mechanism of hydrogen exchange. In 1934, Ingold et al. [6] showed that deuterium exchange in the acid medium proceeded by a type of electrophilic substitution. This hypothesis was confirmed on many examples in our laboratory [8], in particular, in the previous paper [1]. In this it was very clearly shown that, if, due to satiation of the free electron pair of the nitrogen atom, the degree of electronegativity of the carbon atoms of the aromatic amine is lowered, and therefore the addition to them of deuterons of the acid becomes less probable, then the exchange reaction is inhibited. This is conclusive evidence that the necessary condition for the exchange reaction with an acid is just this addition of D to the carbon atom of the C–H bond.

On the other hand, for an exchange reaction to occur with a base participating, the latter must protonize the hydrogen of the C–H bond. Here, the free carbanions do not have to form (the same as in the case of free carbonium ions in the reaction with an acid). The fact that in hydrogen exchange catalyzed by a base, the substance is a proton donor is also indicated by the deep analogy between the metallation of aromatic substances by alkaliorganic compounds and hydrogen exchange in a basic medium, as has been noted several times in work from our laboratory [9]. The mechanism of metallation by alkaliorganic compounds has been explained by many papers [16]. From Bryce-Smith's proposal, this mechanism has been given the designation "protophilic." The attack of a nucleophilic reagent is directed not toward the carbon atom of the C–H bond (as occurs in the nucleophilic substitution of H), but toward the H atom. The metal cation is added to the negatively charged carbon atom only in the second stage. The exchange of hydrogen catalyzed by ND_2^- ion proceeds similarly. The ND_2^- ion attracts the hydrogen of the C–H bond in the form of a proton and this allows the D of ND_3 to add to the carbon atom. This process may occur in a single act in an activated complex. Therefore, the similarity between the laws of metallation and hydrogen exchange in ammoniacal alkali for anisole are understandable. In the opinion of Roberts [7], the primary attack of the ND_2^- ion does not involve the π-electron system of the ring, as occurs in nucleophilic aromatic substitution.

The hypothesis on the mechanism of exchange reactions presented is supported by ideas [9, 17] on the effect of the charge of the substance on the rate of hydrogen exchange, which have received further confirmation in this work.

We plan to supplement our investigations with data on hydrogen exchange in aromatic amines with solutions of potassamide in liquid ammonia and on deuterium exchange with DF and DF + BF_3 in aromatic compounds with substituents containing oxygen and nitrogen and also to measure the rate of deuterium exchange of the nonequivalent hydrogen atoms in diphenyl ether.

SUMMARY

1. All the hydrogen atoms in the phenolate ion, diphenyl ether and anisole,exchange with a solution of KND_2 in liquid ND_3. Since the amide ion is a very strong base, the differences in acidity and reactivity in exchange of the nonequivalent hydrogen atoms of the aromatic rings in the substances named were considerably leveled out.

2. Hydrogen in the phenolate ion exchanges at a rate three orders less than in benzene. This is explained by the fact that the negative charge of the ND_2^- ion hinders the approach of the catalyst.

3. The hydrogen in diphenyl ether exchanges considerably more quickly than that in benzene.

4. The rate of hydrogen exchange in anisole falls in the sequence: ortho > meta > para > OCH_3. This order indicates that in contrast to the exchange with an acid, in the exchange of hydrogen in the ring with a base, the main role is played not by the π,p-conjugation effect, but by the inductive effect of the methoxyl group oxygen. The hydrogen of the latter exchanges more slowly than the para atom of the anisole-aromatic ring.

5. Considerations on the mechanism of hydrogen exchange with acids and bases are discussed.

6. Methods are presented for preparing the deuteroanisoles: $C_6D_5OCD_3$,$C_6H_5OCD_3$, 2,4,6-$C_6D_3H_2OCH_3$, 3,5-$C_6D_2H_3OCH_3$ and p-$C_6DH_4OCH_3$, using exchange reactions in various solvents.

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ISOTOPE EXCHANGE OF 2-MERCAPTOBENZTHIAZOLE SULFUR AND ELEMENTARY SULFUR IN THE PRESENCE OF AMINES

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In investigations published previously [1-3], it was shown that vulcanization accelerators react with sulfur during rubber vulcanization. It was established experimentally, using radioactive isotopes, that there is a rapid isotope exchange of sulfur atoms between the accelerators and the materials being vulcanized, during rubber vulcanization. It was found that the more efficient the accelerator, the lower the temperature at which the isotope exchange of sulfur atoms occurred and the greater the rate [4].

It is known that amines were the first organic accelerators used in the rubber industry [5] and that they are still important in the technology of rubber preparation. The addition of amines to the rubber raises the activity and efficiency of the sulfur-containing, organic rubber vulcanization accelerators.

Elucidation of the effect of amines on the rate of isotope exchange of sulfur atoms of the most widely used accelerator, 2-mercaptobenzthiazole (Captax), and the vulcanization agent, elementary sulfur, is of both practical and theoretical value. If the hypothesis on the correlation between vulcanization rate and isotope-exchange rate is correct, then a more rapid sulfur exchange may be expected in the presence of amines.

EXPERIMENTAL

A study was made of the effect of tertiary (triethylamine) and secondary (dipropylamine and diamylamine) amines on the exchange of sulfur atoms between 2-mercaptobenzthiazole and elementary sulfur over a wide temperature range.

2-Mercaptobenzthiazole and radioactive sulfur (S^{35}) were used in equimolecular amounts. The amines were introduced into the reaction medium in amounts of 0.1 to 1.0 parts relative to the amount of accelerator.

The experiments were performed in sealed ampoules in naphthalene solution, in approximation of the rubber system. Into the ampoules was placed 0.08 g of 2-mercaptobenzthiazole and 0.0153 g of radioactive sulfur, dissolved in 2.29 g of naphthalene. The amines were added before the ampoules were sealed. The sealed ampoules were kept for five minutes on a water bath to dissolve the accelerator and the sulfur in the naphthalene completely, and then heated in a thermostat under strictly defined temperature conditions. After being heated, the ampoules were opened, 5 ml of toluene added to the contents, and the ampoules placed in a beaker with boiling water until the whole mass dissolved. The solution was then poured into a separating funnel in which was placed 10 ml of 1% sodium hydroxide solution. The mercaptobenzthiazole passed into the aqueous layer as the sodium salt and the radioactive sulfur remained in the layer of organic solvent. The mercaptobenzthiazole and sulfur were thus separated.

The addition of hydrochloric acid to the alkaline solution liberated the mercaptobenzthiazole, which was recrystallized several times until its melting point reached 176-178°. The mercaptobenzthiazole, isolated after the exchange reaction, was examined for radioactivity by the procedure described previously [6], using an end-window counter for soft β-radiation. The percentage of sulfur-isotope exchange was calculated on the basis of the fact we demonstrated experimentally, that only the sulfur of the mercaptobenzthiazole sulfhydryl group participates in the isotope exchange [7].

We studied the isotope exchange of sulfur atoms at temperatures of 100, 120 and 140°, i.e., at temperatures at which rubber mixtures and their vulcanizates are prepared.

Isotope Exchange of 2-Mercaptobenzthiazole Sulfur and Elementary Sulfur in the Presence of Amines

Experimental conditions		Initial radioactivity of sulfur (counts/mg per 5 min) (S*)	Theoretical number of counts at complete exchange per mg of sulfur	Exptl. No. of counts per mg of sulfur in mercaptobenzthiazole	Percent exchange			
time (in min)	temperature				without amines	dipropylamine	diamylamine	triethylamine
90	100°	9949	4975	98	1.9	—	—	—
				490	—	9.8	—	—
				355	—	—	7.1	—
				855	—	—	—	17.4
240	100	10160	5080	324	6.3	—	—	—
				897	—	17.6	—	—
				621	—	—	12.2	—
				1107	—	—	—	21.8
360	100	998	499	105	21	—	—	—
				242	—	48	—	—
				252	—	—	—	50.6
60	120	1035	517	137	26	—	—	—
				203	—	39	—	—
				203	—	—	39	—
				208	—	—	—	40.5
120	120	1367	683	279	41	—	—	—
		9631	4810	2442	—	—	50.7	—
				2645	—	—	—	54.9
240	120	1411	705	437	62	—	—	—
		9419	4710	4679	—	99.3	—	—
		9737	4869	3816	—	—	78.3	—
				3857	—	—	—	79.2
360	120	9313	4656	3837	82	100	100	100
30	140	1173	587	363	62	—	—	—
				555	—	95	—	—
				563	—	—	96	—
60	140	1352	676	476	70	100	100	100
90	140	1061	5[illegible]0	742	100	100	100	100

Analysis of the experimental data given in the Table showed that the exchange of sulfur atoms increased sharply in the presence of minute quantities of amines. It is interesting to note the fact that the strongest acceleration of the isotope exchange of sulfur atoms in the presence of amines was observed at 100°, i.e., at the temperature at which rubber is mixed with the ingredients and there is the greatest danger of premature scorching in the rubber mixtures. It is well known in technological practice that cases of premature scorching of rubber mixtures during their preparation or storage are most common in the presence of sulfur-containing accelerators and amine activators. Acceleration of isotope exchange was also observed at 120 and 140°, i.e., at conditions of technical vulcanization; in the presence of amine at 140°, complete exchange was achieved in approximately 30 minutes, while without amines it occurred only after 90 minutes.

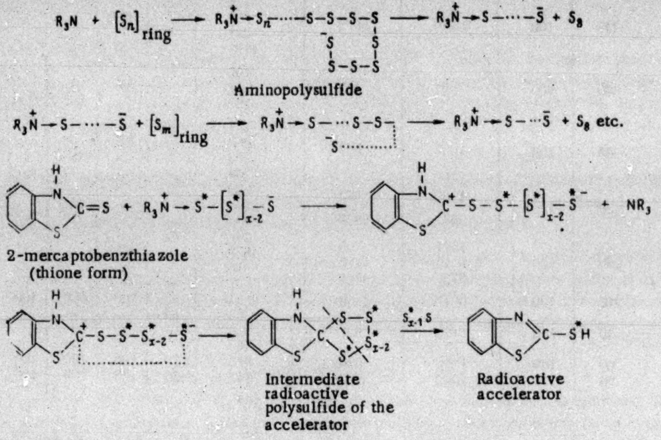
The experimental data obtained do not, however, allow us to differentiate between the effect on the isotope-exchange rate of the secondary and tertiary amines investigated. The data obtained agree well with those in [8], which demonstrated that the isotope exchange of 2-mercaptobenzthiazole sulfur with elementary sulfur was accelerated by the presence of a sulfur-free nitrogen-containing accelerator – diphenylguanidine (DPG). It is known that the use of the combination of accelerators, mercaptobenzthiazole–diphenylguanidine, has a greater accelerating effect than the action of each accelerator separately.

Thus one may conclude that amines, which accelerate the action of sulfur-containing accelerators, also accelerate isotope exchange of sulfur atoms of the accelerators and the vulcanizing agents.

How can one explain the acceleration of isotope exchange of sulfur atoms in the presence of amines? It is known that amines have a catalytic effect on the allotropic changes of sulfur [9]. There is reason to believe that the insoluble modifications of sulfur consist of high-molecular rings and not of chains [10]. This ring must be broken at some place to convert the insoluble to a soluble sulfur modification. The energy of the simple

S–S bond in the ring was evaluated as 63.8 kcal per mole, i.e., very great. The sulfur rings may be broken either thermally or catalytically. The basic amines are an active group of catalysts, which convert high-molecular sulfur atom rings to eight-membered rings. It is known that the insoluble form of sulfur dissolves almost instantaneously in benzene or carbon disulfide if it is shaken with a drop of amine [11] to form the intermediate aminopolysulfide. According to Krebs [9], the rate at which insoluble sulfur converts to soluble sulfur may best be explained on the basis of chain-reaction principles.

Both ends of the broken sulfur ring are extremely reactive and may behave ionogenically. Under the effect of the aminopolysulfide formed, the chain reaction continues until the ends of the same sulfur ring react with each other to form a ring or with another component (in our case, with the accelerator). The activation of sulfur by the action of amines to form aminopolysulfides and eight-membered sulfur rings may be represented by the following scheme:


Aminopolysulfide
2-mercaptobenzthiazole (thione form)
Intermediate radioactive polysulfide of the accelerator
Radioactive accelerator
etc.

On reacting with the active forms of the accelerator, the aminopolysulfides decompose to form an unstable intermediate polysulfide compound of the accelerator. The decomposition of the polysulfide accelerator formed results in the exchange of sulfur atoms and the liberation of active sulfur, which reacts chemically with the molecular structure of the rubber.

It should also be noted that the accelerating action of sulfur-free, amino-containing accelerators of rubber vulcanization is based on the formation of aminopolysulfides and their decomposition with the liberation of active sulfur. On the other hand, reaction with the basic amines converts mercaptobenzthiazole to an ionic form, which reacts with aminopolysulfide to form an intermediate polysulfide complex, also, and during its decomposition,isotope exchange of sulfur atoms occurs.

Thus, under the action of amines, the bonds between the atoms in sulfur rings are broken heterolytically and this accelerates the formation of an intermediate polysulfide compound of the accelerator, which decomposes with exchange of sulfur atoms.

We are grateful to E.N. Gur'ianova for her help in carrying out this investigation.

SUMMARY

1. A study was made of the kinetics of the exchange between 2-mercaptobenzthiazole sulfur and elementary sulfur in the presence of the amines, dipropylamine, diamylamine and triethylamine at 100, 120 and 140°.

2. It was shown that amines accelerate isotope exchange of the sulfur atoms of the rubber-vulcanization

accelerator, 2-mercaptobenzthiazole (Captax), and elementary sulfur, which agrees well with the technological practice of efficient rubber vulcanization in the presence of amines.

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DEHYDROGENATION KINETICS OF CYCLOHEXANE AND ITS HOMOLOGS ON A CHROMIUM CATALYST AT ATMOSPHERIC PRESSURE

G.N. Maslianskii and N.R. Bursian

The dehydrogenation of six-membered naphthenes on oxide catalysts at atmospheric pressure has been studied by many authors and a large amount of experimental material has been accumulated in this field [1]. The reaction kinetics of cyclohexane dehydrogenation on a chromium catalyst were first studied by A.A. Balandin and N.N. Brusov [2] and also by B.L. Moldavskii, et al. [3]. Later, the dehydrogenation of six-membered naphthenes on chromium catalysts was studied in other works by A.A. Balandin, et al. [4-6]. The kinetics of the same reaction were also studied by other authors [7-10]. Despite this, some data on the kinetics of cyclohexane dehydrogenation are contradictory. Thus, the investigations of M.Ia. Kagan, et al. [7-9], show that the rate of the dehydrogenation reaction is inversely proportional to the concentration of hydrogen in the gas phase. Starting from this, a kinetic equation was set up, allowing for inhibition of the reaction by hydrogen.

On the other hand, E.F. Herrington and E.K. Rideal [10] came to the conclusion that in the dehydrogenation of cyclohexane on a Cr_2O_3/Al_2O_3 catalyst, the benzene and hydrogen acted as diluents and had no inhibiting action on the reaction. Thus, while the data of the authors mentioned on the effect of benzene on the reaction kinetics of cyclohexane dehydrogenation agree, the data with regard to hydrogen are contradictory.

According to the data of different authors, the value of the apparent activation energy of cyclohexane dehydrogenation on different chromium catalysts varies over the range of 26,000-40,700 cal/mole [2, 3, 8, 10].

In the present work* a study was made of the dehydrogenation kinetics of cyclohexane on an alumino-chromium catalyst (Cr_2O_3/Al_2O_3) at atmospheric pressure. In addition, measurements were made on the relative dehydrogenation rates of some cyclohexane homologs (methylcyclohexane, 1,3-dimethylcyclohexane, 1,3,5-trimethylcyclohexane and isopropylcyclohexane).

Further investigations, devoted to studying the reaction kinetics of cyclohexane dehydrogenation on oxide catalysts at elevated pressures, will be reported in later communications.

EXPERIMENTAL

Procedure and Starting Materials

Cyclohexane and its homologs were prepared by hydrogenating the appropriate aromatic hydrocarbons over a nickel catalyst. The characteristics of the hydrocarbons used in the work are given in Table 1.

The experiments were performed in a flow apparatus.

The reactor was a glass tube placed vertically in an electric furnace. The catalyst (20 ml) was placed in a constant temperature zone. During the experiments the temperature was maintained with an accuracy of ±1°.

The hydrocarbon was fed steadily into the reactor from a graduated burette. The reaction products emerging from the reactor were passed into a condenser. The condensed hydrocarbons were collected in a receiver. The gaseous reaction products were collected in graduated burettes.

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*Dissertation work of N.R. Bursian, completed in 1947.

TABLE 1

Name of hydrocarbon	Present work			Literature data [11]		
	boiling point (760 mm)	n_4^{20}	d_4^{20}	boiling point (760 mm)	n_D^{20}	d_4^{20}
Cyclohexane	80.8°	1.4262	0.7781	80.75°	1.4262	0.7786
Methylcyclohexane	100.8	1.4232	0.7694	100.93	1.4231	0.7694
Ethylcyclohexane	131.3	1.4332	0.7884	131.78	1.4330	0.7879
Dimethylcyclohexane (mixture of isomers)	120—124	1.4252	0.7701	—	—	—
1,3,5-Trimethylcyclohexane	138—139.5	1.4283	0.7761	140.4—140.9*	1.4277 *	0.7765 *
				138—139 **	1.4251 **	0.7720 **
Isopropylcyclohexane	152—155	1.4400	0.7983	154.56	1.4409	0.8022

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*Cis-isomer.

**Trans-isomer.

The duration of an experiment was usually two to three hours. Every five minutes readings were taken of the amount of hydrocarbon introduced, the temperature and the amount of gas liberated. The rate of hydrogen liberation and the agreement of the refractive indexes of catalyzate samples indicated the constancy of the catalyst activity with time. In addition, control experiments with cyclohexane were performed periodically during the course of the whole series of experiments. If a fall in the catalyst's activity was observed, then it was regenerated with air. The regeneration conditions were chosen on the basis of special work and gave good reproducibility of catalyst activity [12].

It was established that in the dehydrogenation of cyclohexane, the catalyzates obtained contained insignificant amounts of unsaturated hydrocarbons; therefore, it was possible to determine the benzene content from the refractive index [13] on the one hand, and from the amount of hydrogen liberated on the other.

In contrast to the dehydrogenation products of cyclohexane, the catalyzates obtained by dehydrogenating its homologs contained noticeable amounts of unsaturated hydrocarbons. Due to this, the amount of aromatic hydrocarbons was determined by a dispersion method [14]. The appropriate measurements were performed on a Pulfrich refractometer. The content of unsaturateds was calculated from the bromine number, which was determined by the method of Francis [15].

The catalyst was prepared by coprecipitation of chromium and aluminum hydroxides. The prepared, baked catalyst contained 20% of Cr_2O_3 and 80% of Al_2O_3.

Kinetics of Cyclohexane Dehydrogenation on a Chromium Catalyst

The dehydrogenation kinetics of cyclohexane were studied at 410-475°.

We used the equation developed by A.V. Frost [16] to describe the kinetics of the reaction studied.

If we consider that the catalyst surface is uniform and that the adsorption of the starting material and the reaction products is governed by the Langmuir equation, then the reaction rate, expressed as the number of moles reacting in unit time on unit surface, will equal:

$$\frac{\partial^2 x}{\partial t \partial S} = \frac{k_1 b_1 P_1}{1 + b_1 P_1 + b_2 P_2 + \ldots\ldots b_i P_i}, \tag{1}$$

where k_1 is the rate constant of the surface reaction, relative to 1 cm^2 in unit time, b_1, b_2 and b_i are the adsorption coefficients of the substances and P_1, P_2 and P_i are the partial pressures corresponding to these substances at a moment of time when the degree of conversion has reached a value $\underline{y}$.

Transposition and integration of this equation gives the following expression for the rate constant of a monomolecular, heterogeneous, catalytic reaction, occurring in a flow system and inhibited by the reaction products:

TABLE 2

The Effect of the Rate of Input of Cyclohexane on Its Degree of Dehydrogenation (Chromium catalyst – sample 1, 450°)

Expt. No.	Cyclohexane input		Amt. of gas (in ml) liberated in 5 min	n_D^{20} of catalyzate	Percent of dehydrogenation			$\alpha \cdot 10^3$ (mole per min)
	ml/hr	m mole/ per min			from gas	from n_D^{20}	average	
1	60.0	9.2	416	1.4335	13.4	13.8	13.6	0.26
2*	29.6	4.56	302	1.4375	19.7	20.5	20.1	0.24
3	15.0	2.31	231	1.4445	29.7	32.3	31.0	0.24
4*	30.0	4.62	309	1.4365	19.9	18.8	19.3	0.22
5	5.5	0.85	140	1.4595	48.8	54.0	51.4	0.25
6*	30.0	4.62	298	1.4365	19.2	18.8	19.0	0.22
7	3.0	0.46	106	1.4700	68.0	67.5	67.8	0.25
8*	30.0	4.62	323	1.4380	20.8	21.3	21.0	0.25

*Control experiments.

TABLE 3

The Effect of Reaction Temperature on the Rate of Cyclohexane Dehydrogenation (Chromium catalyst – sample 1)

Exptl. conditions			Amt. of gas (in ml) liberated in 5 min	n_D^{20} of catalyzate	Percent of dehydrogenation			$\alpha \cdot 10^3$ (mole per min)
temperature	cyclohexane input				from gas	from n_D^{20}	average	
	ml/hr	m mole/ per min						
450°	30.0	4 62	323	1.4380	20.8	21.3	21.0	0.25
410	7.2	1.11	65	1.4370	17.4	19.8	18.6	0.05
430	15.0	2.31	152	1.4370	19.4	19.8	19.6	0.11
450	30.0	4.62	320	1.4380	20.6	21.3	20.9	0.25
475	60.0	9.2	490	1.4404	26.2	25.8	26.0	0.7
450	30.0	4.62	309	1.4365	19.9	18.8	19.3	0.22

$$\alpha = v_0 \ln \frac{1}{1-y} - \beta v_0 y, \qquad (2)$$

where α is a value proportional to the reaction rate constant, v_0 is the number of moles of starting material introduced per minute, y is the degree of conversion of the starting material, and β is a value, characterizing the constancy of the ratio of the adsorption coefficients.

At constant temperatures and pressures, the values α and β do not depend on v_0 and y; consequently, Equation (2) gives a straight line in the coordinates $v_0 y$ and $v_0 \ln \frac{1}{1-y}$.

To elucidate the effect of the volume rate on the course of the reaction, a series of experiments was performed at 450°. The cyclohexane input was varied over the wide limits from 3 to 60 ml per hour, i.e., by a factor of 20; the degree of conversion changed from 13.6 to 67.8%, respectively. The experimental results are given in Table 2. The constancy of the catalyst's activity was confirmed quite satisfactorily by the reproducibility of control experiments.

The values of $v_0 \ln \frac{1}{1-y}$ and $v_0 y$, calculated from Equation (2) for the experiments in Table 2, lie well on a straight line. Calculating by the method of least squares, it was found that $\alpha = 0.24 \cdot 10^{-3}$, $\beta = 0.86$.

The deviations of the values calculated for separate experiments from the value given above, did not exceed the limits of error of the experiment.

To establish the dependence of reaction rate on temperature, a series of experiments was performed at 410-475° and the results are given in Table 3. A plot of log α against 1/T gave a straight line, which was described by the equation:

$$\log \alpha = 8.8 - \frac{8960}{T}. \qquad (3)$$

The value of the apparent activation energy, calculated from Equation (3) was 41,000 cal/mole.

The applicability of Equation (2) to the reaction studied indicates that the reaction rate increases as the partial pressure of cyclohexane increases and that it is inhibited by the reaction products.

To elucidate the effect of benzene on the course of the reaction, a series of experiments was carried out with mixtures of benzene and cyclohexane in equal amounts at 450°. The results of the experiments are given in Table 4.

TABLE 4

Experiments on the Dehydrogenation of Cyclohexane Mixed With Benzene (Chromium catalyst – sample 1, 450°)

Exptl. conditions			Amt. of gas (in ml) liberated in 5 minutes	n_D^{20} of catalyzate	Percent of cyclohexane dehydrogenated		
comp. starting mixture (in mole %)		mixture input (mmole per min)			from gas	from n_D^{20}	average
C_6H_{12}	C_6H_6						
100	—	4.62	319	1.4380	20.5	21.3	20.9
89.3	10.7	4.69	305	1.4430	21.6	21.6	21.6
80.2	19.8	4.82	254	1.4470	19.6	20.6	20.1
67.7	32.3	4.88	239	1.4532	21.6	19.5	20.5
40.2	59.8	5.14	147	1.4696	21.2	18.2	19.7
100	—	4.62	319	1.4380	20.5	21.3	20.9

On changing the molar concentration of benzene in the mixture from 10.7 to 59.8%, the degree of conversion of cyclohexane remained practically constant. Consequently, benzene does not slow down the dehydrogenation of cyclohexane on a chromium catalyst and is only a diluent.

The problem of the effect of hydrogen on the reaction kinetics of cyclohexane dehydrogenation were studied in an investigation of this reaction under a pressure of hydrogen.* It was established that the reaction was inhibited by hydrogen.

Thus, our data agree with the data of M.Ia. Kagan [7] and contradict the results obtained by Herrington and Rideal [10].

A Study of the Relative Dehydrogenation Rates of Six-Membered Naphthenes on a Chromium Catalyst

For studying the relative dehydrogenation rates, we chose six-membered naphthene hydrocarbons, which differed both in the number and the character of the substituent groups on the hexamethylene ring. We used the following hydrocarbons: cyclohexane, methylcyclohexane, dimethylcyclohexane (a mixture of isomers), 1,3,5-trimethylcyclohexane, ethylcyclohexane and isopropylcyclohexane.

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*The results of the investigation will be put into the next communication.

TABLE 5

Experiments on the Dehydrogenation of Different Six-Membered Naphthenes (Chromium catalyst – sample 2, 450°)

Hydrocarbon input		Catalyzate characteristics		Catalyzate composition (wt. %)		Degree of conversion (100 y) (in mole %)	$\alpha \cdot 10^3$ (mole/min)
ml/hr	m mole/per min	bromine number	δ_{Fc}^{*}	unsaturateds	aromatics		
Cyclohexane							
29.6	4.57	6.3	106.5	3.2	11.4	15.5	0.25
14.2	2.18	7.5	112.7	3.8	18.2	23.0	0.25
5.5	0.93	7.5	123.1	3.8	20.5	34.8	0.25
Methylcyclohexane							
29.2	3.82	5.0	112.3	3.0	16.6	20.2	0.36
15.0	1.96	4.0	119.3	2.4	25.0	28.6	0.36
5.0	0.66	5.3	133.0	3.2	40.9	45.6	0.33
Dimethylcyclohexane (mixture of isomers)							
31.0	3.58	4.3	114.2	3.0	18.5	22.4	0.42
14.4	1.65	4.5	124.9	3.1	32.0	36.3	0.47
5.8	0.66	4.3	136.2	3.0	46.1	50.5	0.42
Ethylcyclohexane							
29.5	3.46	5.3	115.2	3.6	21.2	25.8	0.50
14.4	1.69	5.5	122.9	3.8	30.8	35.7	0.47
6.5	0.76	5.5	133.7	3.8	44.1	49.3	0.44
Isopropylcyclohexane							
30.0	3.16	3.2	116.3	2.5	25.2	28.7	0.55
15.6	1.65	4.7	121.9	3.6	32.0	36.8	0.50
7.0	0.74	5.5	135.2	4.3	48.4	53.8	0.53
1,3,5-Trimethylcyclohexane							
30.0	3.08	3.9	119.1	3.0	23.9	27.8	0.53
21.6	2.22	4.5	123.4	3.5	29.2	33.6	0.55
14.6	1.50	4.1	128.8	3.2	36.2	40.5	0.53

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*Specific dispersion at 20°.

For each naphthene hydrocarbon we performed a series of three experiments, which differed in the input-volume rate of the hydrocarbon. To check the stability of the catalyst, each series of experiments was begun and ended with a control experiment with cyclohexane.

The results of the experiments with different six-membered naphthenes are given in Table 5.

The catalyzates obtained by dehydrogenating the naphthenes studied contained unsaturated hydrocarbons together with the aromatics. The amount of the former, however, was small and varied over the range of 2 to 4% by weight.

The degree of conversion presented in Table 5 (y) was calculated in the following way: the aromatic and unsaturated hydrocarbon contents of the catalyzates were expressed in molar percents and then the values obtained were added.

The reaction-rate constants were calculated by Equation (2), as in experiments with cyclohexane. The constant α was found to be quite invariant in each of the series of experiments with the hydrocarbons studied.

The average values of the reaction-rate constants ($\alpha \cdot 10^3$) for the dehydrogenation of six-membered naphthenes at 450° on a chromium catalyst, from the data in Table 5, are given below.

Cyclohexane	0.25	Ethylcyclohexane	0.47
Methylcyclohexane	0.35	1,3,5-Trimethylcyclohexane	0.54
Dimethylcyclohexane	0.44	Isopropylcyclohexane	0.53

If we consider that the rate of cyclohexane dehydrogenation equals unity, then the relative rates of dehydrogenation of its homologs equal:

Cyclohexane	1	Ethylcyclohexane	1.9
Methylcyclohexane	1.4	1,3,5-Trimethylcyclohexane	2.2
Dimethylcyclohexane (mixture of isomers)	1.8	Isopropylcyclohexane	2.1

Thus, one can conclude that with an increase in the molecular weight of six-membered naphthene hydrocarbons, the rate of their dehydrogenation on a chromium catalyst increases regularly.

SUMMARY

1. A study was made of the reaction kinetics of cyclohexane dehydrogenation on a chromium catalyst at 410-475° and atmospheric pressure.

2. It was established that the rate of the dehydrogenation reaction was described by the kinetic equation for a monomolecular reaction,and inhibited by the products of the latter.

3. It was shown that benzene did not slow down the reaction.

4. It was found that the rate of dehydrogenation of six-membered naphthenes increased regularly with an increase in the hydrocarbon's molecular weight.

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A STUDY OF THE DEHYDROGENATION OF CYCLOHEXANE ON A CHROMIUM CATALYST UNDER A PRESSURE OF HYDROGEN

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The success of the industrial application of the catalytic aromatization of hydrocarbons over the last twenty years is closely connected with the realization of this process at an elevated pressure and in the presence of hydrogen [1, 2]. Despite this, very few works [3-5] have been devoted to studying the aromatization of individual hydrocarbons on oxide catalysts at elevated pressures. The kinetics of dehydrogenation of six-membered naphthenes on these catalysts under a pressure of hydrogen, in general, has been studied little.

The aim of the present work was to study the kinetic laws of cyclohexane dehydrogenation on a (Cr_2O_3/Al_2O_3) chromium catalyst at an elevated pressure.*

It was established that the reaction rate was proportional to the partial pressure of cyclohexane in the range from 0.5 to 4.0 atm.

On the other hand, increasing the partial pressure of hydrogen caused a sharp fall in the rate of cyclohexane dehydrogenation. Since the effect of hydrogen pressure was studied under conditions at which the concentrations of the reacting materials were far from equilibrium, one may conclude that the reason for the inhibition of the reaction by hydrogen is connected with the kinetics of the reaction studied. The facts established allow the reaction rate of cyclohexane dehydrogenation at elevated pressures to be expressed by a kinetic equation, allowing for inhibition of the reaction by hydrogen.

The investigations showed that the kinetics rules, established for the dehydrogenation of cyclohexane on a chromium catalyst at atmospheric pressure [6], remain accurate when the reaction is performed at pressures of up to 20 atm.

It is noteworthy that despite the fact that the chromium catalyst used showed a high activity in operation at atmospheric pressure [6], the degree of cyclohexane conversion in experiments with a pressure of hydrogen was small, although the reaction temperature exceeded 500°. Greensfelder, et al., [5] also observed a sharp fall in hydrocarbon aromatization when the same reaction was performed over a chromium catalyst under a pressure of hydrogen.

Analysis of the results obtained showed that the low degree of cyclohexane conversion in experiments under pressure cannot be ascribed to inhibition of the reaction by hydrogen alone, but is also connected with deactivation of the catalyst during its preliminary treatment with hydrogen, which was performed at 550° and a pressure of 20 atm [7].

Thus, in an experiment at atmospheric pressure and 475° with a cyclohexane input of 0.46 mole/min per liter of catalyst, 26% of the cyclohexane reacted [6]. On the other hand, calculation** showed that under the same conditions, not more than 2% of the cyclohexane should be converted on the portion of catalyst used in experiments under pressure. Thus, portions of the same sample of catalyst, used in experiments at atmospheric and elevated pressures, differed sharply in activity.

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*Dissertation work of N.R. Bursian, completed in 1947.

**The calculation was carried out using formula (3) (see next page) and the experimentally found value of the apparent activation energy of cyclohexane dehydrogenation. It was assumed that P = 1 atm and $\alpha = 0$.

A similar deactivation is apparently one of the reasons for the extremely limited use of chromium catalyst in present-day aromatization processes [2], which, as mentioned above, are performed under a pressure of hydrogen.

EXPERIMENTAL

Procedures and Starting Materials

The experiments were performed in a flow-type apparatus, which could operate at high temperatures and pressures [9]. The catalyst was prepared by coprecipitation of chromium and aluminum hydroxides. The prepared, baked catalyst contained 20% Cr_2O_3 and 80% Al_2O_3. The cyclohexane was prepared by hydrogenation of benzene over a nickel catalyst.

B.p. 80.8° (760 mm), d_4^{20} 0.7781, n_D^{20} 1.4262. Literature data [8]: b.p. 80.75°(760 mm), d_4^{20} 0.7786, n_D^{20} 1.4262.

The stability of the catalyst was tested by means of control experiments. When a fall in the activity of the catalyst was observed, the catalyst was regenerated. The regeneration was realized by passing air through the catalyst at 550°.

After regeneration, the catalyst was reduced with hydrogen at 550° and 20 atm pressure. The volume rate of hydrogen input was 1000.

Catalyzates obtained in experiments under pressure contained some unsaturateds. Due to this, the amount of aromatic hydrocarbons was determined by a dispersion method [10]. The appropriate measurements were performed on a Pulfrich refractometer. The unsaturated hydrocarbon content was calculated from the bromine numbers [11].

Derivation of Kinetic Equation

The kinetics of cyclohexane dehydrogenation on a chromium catalyst were studied over the range 505-550° and at partial hydrogen pressures not exceeding 20 atm. As was shown by V.R. Zharkova and A.V. Frost [12], under these conditions the equilibrium of this reaction is completely displaced toward benzene.

Analysis of the experimental data showed that the reaction rate may be expressed by an equation, allowing for inhibition of the reaction by hydrogen

$$w = \frac{k \cdot P_{C_6H_{12}}}{1 + bP_{H_2}}, \tag{1}$$

where w is the reaction rate expressed in the number of moles reacting in one minute on unit catalyst surface, k is the reaction constant, $P_{C_6H_{12}}$ and P_{H_2} are the partial pressures of cyclohexane and hydrogen and b is a coefficient equal to 0.2.

The equation was transposed and integrated as A.V. Frost [13] did for the kinetic equation he deduced.

Substituting the values of $P_{C_6H_{12}}$ and P_{H_2} in Equation (1), we obtain

$$w = \frac{k(1-y)P}{1 + \alpha(1+bP) + 3(1+bP)y}, \tag{2}$$

where P is the total pressure in the reactor; y is the degree of cyclohexane conversion and α is the molar ratio of hydrogen : cyclohexane.

As a result of integrating, we find:

$$S \cdot k = k' = v_0 \frac{1+bP}{P}\left[\left(\frac{1}{1+bP} + \alpha + 3\right)\ln\frac{1}{1-y} - 3y\right], \tag{3}$$

where S is the total surface of the catalyst in the reactor.

In determining the degree of conversion y, the portions of cyclohexane converted into benzene and unsaturated hydrocarbon were added together.

We should note that despite the fact that the experiments under pressure were performed at high temperatures, the catalyzates contained practically only cyclohexane besides the aromatic and unsaturated hydrocarbons. Thus, when the catalyzates were treated with 98% sulfuric acid, the physical constants of the unreacted part of the catalyzate agreed with those of the starting cyclohexane.

TABLE 1

Effect of Volume Rate and Temperature on the Dehydrogenation of Cyclohexane (Chromium catalyst – sample 1)

Exptl. conditions				Analysis results (in wt. %)		Cyclohexane reacted (mole %)	$k' \cdot 10^9$
temperature	operating pressure (atm)	C_6H_{12} input (mmoles per min)	molar ratio of $H_2:C_6H_{12}$	unsaturateds	aromatics		
550°	6	24.64	4.5	5.5	6.3	12.2	6.0
550	6	12.32	4.2	6.5	15.2	22.7	5.8
550	6	6.16	3.4	6.9	33.8	42.3	5.7
505	6	12.32	4.4	3.8	1.8	5.4	1.2
505	6	6.16	4.3	5.3	7.9	13.8	(1.6)
505	6	3.08	3.8	6.2	11.0	18.0	1.2
505	11	3.85	9.7	3.3	6.5	10.4	1.25
520	11	6.16	9.9	4.5	6.2	11.2	2.2
535	11	9.8	10.0	3.5	7.0	11.4	3.6
550	11	15.7	9.8	4.9	6.4	11.8	5.9

TABLE 2

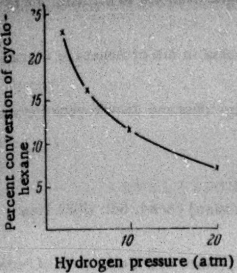
Effect of Cyclohexane Partial Pressure (Chromium catalyst – sample 1, 520°)

Experimental conditions					Analysis results (in weight %)		Cyclohexane reacted (mole %)	$k' \cdot 10^9$
operating pressure (atm)	C_6H_{12} input (mmole per min)	molar ratio $H_2:C_6H_{12}$	partial pressure (in atm)		unsaturateds	aromatics		
			C_6H_{12}	H_2				
6	6.16	4.7	1.0	5.0	3.5	10.2	14.5	1.9
5.5	3.08	8.5	0.6	4.9	4.9	12.7	18.5	2.3
8	18.48	1.5	3.2	4.8	4.4	9.4	14.5	2.0
9	24.64	1.2	4.1	4.9	4 4	9.5	14.5	2.1
6	6.16	4.8	1.0	5.0	4.6	9.4	14.8	2.0

The effect of volume rate and temperature was studied at a pressure of 6 atm. Examination of the data presented in Table 1 shows that with a decrease in the volume rate, the benzene content of the catalyzate rapidly increased. Simultaneously, there was also an increase in the unsaturated hydrocarbon content, but considerably more slowly. At low degrees of cyclohexane conversion, the amount of unsaturated hydrocarbon formed noticeably exceeded the amount of benzene. With an increase in the degree of conversion, the ratio between the unsaturated hydrocarbon and benzene sharply decreased.

Using the data in Table 1, we calculated the constants k', which remained quite steady while the degree of conversion changed from 5.4 to 42.5%.

To elucidate the effect of temperature on the rate of dehydrogenation, experiments were performed at temperatures of 505, 520, 535 and 550° and a pressure of 11 atm.



Effect of hydrogen pressure on the rate of cyclohexane dehydrogenation.

The average values of the reaction-rate constant gave a good straight line for a plot of log k' against 1/T.

The value found for the apparent activation energy of cyclohexane dehydrogenation on a chromium catalyst was 45,000 cal/mole, i.e., close to the value obtained in experiments at atmospheric pressure [6].

The effect of cyclohexane partial pressure on the reaction rate was studied at 520°. The partial pressure of cyclohexane was varied over the range from 0.6 to 4.1 atm, while the partial pressure of hydrogen was kept constant.

The results obtained are given in Table 2 and show that with a simultaneous and proportional increase in the cyclohexane partial pressure and the volume rate of hydrocarbon input, the degree of conversion remained practically constant. This indicates that the reaction rate is proportional to the partial pressure of cyclohexane.

The fact indicated is reflected in kinetic equation (1), according to which, at a constant hydrogen partial pressure, the reaction rate should increase proportionally to the increase in the cyclohexane partial pressure. The applicability of Equation (1) is confirmed by the fact that the rate constants, calculated by Equation (3), remained quite constant when the cyclohexane partial pressure was changed from 0.6 to 4.1 atm (Table 2).

The effect of hydrogen partial pressure on the reaction rate was studied in a series of experiments at 520°. The experiments were performed at practically constant cyclohexane partial pressure. The hydrogen partial pressure was varied over the range from 1.9 to 20 atm. The results of the experiments are given in Table 3 and illustrated in the figure. Examination of these results leads to the conclusion that the aromatic and unsaturated hydrocarbon content of the catalyzates falls sharply with an increase in the hydrogen partial pressure. Correspondingly, the total amount of cyclohexane conversion also decreased. Thus, when a hydrogen partial pressure of from 1.9 to 20 atm was used, the degree of cyclohexane conversion changed from 22.8 to 7.2%. Hence, the dehydrogenation of cyclohexane is inhibited by hydrogen.

TABLE 3

Effect of Hydrogen Partial Pressure (Chromium catalyst – sample 1, 520°)

Experimental conditions					Analysis results (in weight %)		Cyclohexane reacted (mole %)	$k' \cdot 10^3$
operating pressure in atm.	C_6H_{12} input (mmole per min)	molar ratio $H_2 : C_6H_{12}$	partial pressure (in atm) C_6H_{12}	partial pressure (in atm) H_2	unsaturateds	aromatics		
6	6.16	4.5	1.1	4.9	3.8	11.5	16.1	2.0
3	6.16	1.8	1.1	1.9	6.0	15.8	22.8	2.3
11	6.16	9.0	1.1	9.9	3.9	7.2	11.6	2.1
21	6.16	21.0	1.0	20.0	2.9	4.0	7.2	2.4
6	6.16	4.0	1.2	4.8	3.8	11.5	16.1	2.0

As the data in Table 3 show, the reaction-rate constants, calculated by Equation (3), remain quite constant for this series of experiments also.

SUMMARY

1. A study was made of the reaction kinetics of cyclohexane dehydrogenation on a chromium catalyst (Cr_2O_3/Al_2O_3) at 505-550° and at hydrogen pressures of from 1.9 to 20 atm.

2. It was established that when the cyclohexane partial pressure was changed from 0.6 to 4.1 atm, the reaction rate was proportional to the partial pressure of this hydrocarbon.

3. It was found that increasing the hydrogen partial pressure led to a decrease in the cyclohexane dehydrogenation rate.

4. It was established that the value of the apparent activation energy of cyclohexane dehydrogenation was 45,000 cal/mole.

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ALKYLATION OF ISOPROPYLBENZENE BY PSEUDOBUTYLENE IN THE PRESENCE OF $BF_3 \cdot H_3PO_4$

S.V. Zavgorodnii and L.S. Shvetsova

In a previous paper [1] it was shown that the molecular compound $BF_3 \cdot H_3PO_4$ was an extremely efficient catalyst for the alkylation of benzene with pseudobutylene. In developing these investigations, we studied the reaction of isopropylbenzene with pseudobutylene in the presence of the same catalyst.

As the investigations showed, pseudobutylene alkylated isopropylbenzene with much more difficulty than benzene under corresponding conditions and the alkylation products were formed in lower yields. The secondary butyl radical was directed to a large extent into the para position. As a result, a mixture of isopropyl-sec-butylbenzenes was formed, consisting of approximately 91% of the para isomer and 9% of the ortho isomer. The relative amount of these in the alkylate was 68-85%. The optimal alkylation conditions, under which the isopropyl-sec-butylbenzenes were obtained in 62-65% yield and a relative content in the alkylate of 80-84%, were a molar ratio of isopropylbenzene, pseudobutylene and catalyst of 3-3.5 : 1 : 0.2-0.3, a temperature of 50-60° and a pseudobutylene input of 1.6-2.5 liters/hour.

Increasing the amount of catalyst to 0.5 mole under the same conditions lowered the yield of isopropyl-sec-butylbenzenes to 52% of the theoretical and their content in the alkylate to 73%. An alkylation with a ratio of reagents and catalyst of 2 : 1 : 0.3 and a temperature of 50° proceeded similarly. The use of more than 3 moles of isopropylbenzene per mole of pseudobutylene gave isopropyl-sec-butylbenzene yields lower than the optimal, even when 0.4 mole of catalyst was used per mole of pseudobutylene.

Temperature had a noticeable effect on the yield of isopropyl-sec-butylbenzenes and the relative amount of them in the alkylate. This effect was studied at isopropylbenzene, pseudobutylene and catalyst ratios of 2 : 1 : 0.2. The alkylation proceeded very slowly at room temperature. Raising the temperature from 20 to 60° accelerated the alkylation process and increased the yield of isopropyl-sec-butylbenzenes, but lowered their relative content in the alkylate due to the accumulation of polyalkylbenzenes in the alkylate. Thus, for example, at 20, 30-35 and 50-60°, the isopropyl-sec-butylbenzenes were obtained in yields of 18, 47 and 55% of theoretical, respectively, and relative contents in the alkylate of 82, 79 and 76%, respectively. At 100° the pseudobutylene was poorly absorbed in the reaction mixture; the catalyst partially decomposed and gradually lost its activity and the isopropyl-sec-butylbenzenes were obtained in very poor yield.

EXPERIMENTAL

The isopropylbenzene used was the freshly distilled technical product with b.p. 149-150°, d_4^{20} 0.8602, and n_D^{20} 1.4910. The preparation of the other starting materials was described previously [1].

Isopropylbenzene was alkylated with pseudobutylene in the apparatus and by the procedure which was used for the alkylation of benzene [1]. The reaction induction period varied from 15 to 25 minutes. After appropriate treatment and drying, the alkylate was distilled separately for each experiment. The isopropyl-sec-butylbenzene fraction was collected over a range of 4-5°. Then the fractions from all the experiments, presented in the Table, were combined and distilled on a column of 25-30 theoretical plates. The isopropyl-sec-butylbenzenes distilled almost completely at 57.5-58.5° at 2 mm. Oxidation of them with 30% nitric acid gave terephthalic and orthophthalic acids in yields of 46.1 and 4.6%, respectively. The terephthalic acid was identified by converting it to its dimethyl ester and the orthophthalic acid as fluorescein.

Alkylation of Isopropylbenzene With Pseudobutylene in the Presence of $BF_3 \cdot H_3PO_4$

Expt. No.	Molar ratios of isopropylbenzene, pseudobutylene and catalyst	Temperature	Rate of pseudobutylene introduction (liters/hr)	Isopropyl-sec-butylbenzenes	
				yield (in %)	relative percent in alkylate
1	5 : 1 : 0.4	20—30°	1.8	31.0	78.5
2	4 : 1 : 0.4	up to 50	2.5	51.9	72.9
3	4 : 1 : 0.2	50—55	2.5	58.3	81.1
4	3.5 : 1 : 0.2	50—60	3.0	65.5	84.1
5	3 : 1 : 0.5	up to 50	1.2	51.9	72.9
6	3.1 : 0 : 0.25	up to 50	1.6	55.4	74.6
7	3 : 1 : 0.3	50—55	1.6	62.1	80.3
8	3 : 1 : 0.3	30—35	1.7	50.9	75.6
9	3 : 1 : 0.2	50—60	3.4	56.4	85.1
10	3 : 1 : 0.1	up to 30	1.6	12.2	73.7
11	2 : 1 : 0.5	50—55	2.6	46.5	74.3
12	2 : 1 : 0.3	up to 50	1.6	52.8	71.8
13	2 : 1 : 0.2	up to 20	2.4	17.7	81.7
14	2 : 1 : 0.2	30—35	1.8	47.4	78.6
15	2 : 1 : 0.2	50—60	3.0	54.9	76.4
16	2 : 1 : 0.2	80	1.8	49.4	73.3
17	2 : 1 : 0.15	up to 40	2.6	40.9	84.6
18	2 : 1 : 0.1	50—60	2.6	32.3	81.1
19	1 : 1 : 0.5	up to 55	2.0	50.3	70.2
20	1 : 1 : 0.3	30—35	1.6	44.1	70.1
21	1 : 1 : 0.3	up to 55	2.4	56.9	78.0
22	1 : 1 : 0.2	up to 60	2.8	42.4	67.7
23	1 : 1 : 0.1	25—30	3.0	27.1	70.2
24	1 : 1 : 0.1	up to 50	2.4	32.6	78.5

On the basis of these data and the assumption that o- and p-isopropyl-sec.-butylbenzenes have the same tendency for oxidation by 30% nitric acid, we can consider that our product was p-isopropyl-sec.-butylbenzene, containing about 9% of o-isopropyl-sec.-butylbenzene. It was a colorless liquid with a pleasant smell.

d_4^{20} 0.8589, n_D^{20} 1.4876, MR_D 59.14; calc. 58.63. Literature data for isopropyl-sec.-butylbenzene, with the position of the alkyl groups not defined [2]: b.p. 223-227°, d_4^{20} 0.8590, n_D^{20} 1.4910.

Found %: C 88.66, 88.66; H 11.46, 11.38. M 176.5, 174.8. $C_{13}H_{20}$. Calculated %: C 88.55; H 11.45; M 176.3.

After autooxidation of 26.5 g of isopropyl-sec.-butylbenzene (first treated with concentrated sulfuric acid) with atmospheric oxygen in the presence of 1 mg of manganese resinate and 80 mg of calcium hydroxide at 110° for 15 hours, 53.9% of hydroperoxides were determined in the reaction mixture iodometrically. Acid cleavage of these hydroperoxides yielded p-isopropylphenol and methyl ethyl ketone. p-Isopropylphenoxyacetic acid was prepared from the p-isopropylphenol and the 2,4-dinitrophenylhydrazone from the methyl ethyl ketone. The constants of these agreed with literature data. The oxidation products of o-isopropyl-sec.-butylbenzene were not detected.

SUMMARY

A study was made of the alkylation of isopropylbenzene with pseudobutylene in the presence of $BF_3 \cdot H_3PO_4$. The effect of different molar ratios of reagents, catalyst concentrations and temperatures in the range 20-100° on the reaction was demonstrated.

Conditions were found under which isopropyl-sec.-butylbenzene was obtained in 62-65% yield. The mixture of isopropyl-sec.-butylbenzenes contained approximately 91% of p- and 9% of o-isopropyl-sec.-butylbenzene.

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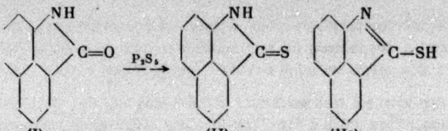
DERIVATIVES OF BENZ-(c,d)-INDOLINE

I. THIONAPHTHOSTYRYL AND N-METHYLTHIONAPHTHOSTYRYL

N.S. Dokunikhin and L.A. Gaeva

The chemistry of benz-(c,d)-indole has been little studied [1]. It has only attracted some attention from investigators recently in connection with determining the structure of lysergic acid – a decomposition product of ergot alkaloids. Unsubstituted benz-(c,d)-indole is unknown. Attempts to synthesize it did not give positive results [2]. Benz-(c,d)-indoline was prepared in 1950 by treating naphthostyryl (I) with $LiAlH_4$ in ethylmorpholine [3]. The latter attracted the attention of investigators as the lactam of 1,8-aminonaphthoic acid – an intermediate in the synthesis of vat dyes of the anthanthrone series [4]. We obtained the thioanalog of naphthostyryl – 2-thionebenz-(c,d)-indoline (II) – previously, by treating 1-naphthyl isothiocyanate with $AlCl_3$ [5]. It seemed interesting to investigate the possibility of another mode of synthesis of this compound and its N-alkyl substituted derivatives, which could not be obtained by isomerization of isothiocyanates.

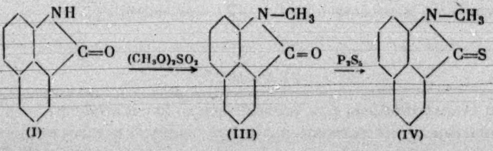
Thionaphthostyryl (II) was obtained from naphthostyryl (I) by heating the latter with P_2S_5 in xylene.



(I) (II) (IIa)

The acid properties shown by thionaphthostyryl indicated that it had the isomeric structure (IIa); however, the infrared spectrum of the crystals showed an absorption band corresponding to NH (ν 3110 cm^{-1}).

Replacement of oxygen by sulfur was also possible for N-methylnaphthostyryl (III). The known method of preparing (III) is by the action of methylamine on 1,8-chloronaphthoic acid [6]. We were able to methylate naphthostyryl directly with dimethyl sulfate in aqueous alkali and with methyl benzenesulfonate in trichlorobenzene.



(I) (III) (IV)

Data on the light absorption of the substances synthesized are given in the Table: solutions in m-xylene were examined on an SF-4 spectrophotometer.

Replacement of the oxygen by sulfur produced an intense absorption band with a maximum at about 435 mμ and the absorption band with a maximum at 320 mμ disappeared.

Substance	λ_{max} m μ	$\varepsilon \cdot 10^{-4}$	λ_{max} m μ	$\varepsilon \cdot 10^{-4}$	λ_{max} m μ	$\varepsilon \cdot 10^{-4}$	λ_{max} m μ	$\varepsilon \cdot 10^{-4}$	λ_{max} m μ	$\varepsilon \cdot 10^{-4}$
(I)			320	0.25	335	0.35	359	0.35		
(II)	290	0.65					360	0.46	434.5	0.95
(III)	290	0.37	320	0.22	335	0.29	370	0.28		
(IV)	300	0.68			343	0.33	360	0.52	435	1.11

EXPERIMENTAL

Thionaphthylstyryl [2-thionebenz-(c,d)-indoline]. 2.5 g of naphthostyryl and 3.2 g of phosphorus pentasulfide in 60 ml of xylene were stirred for three hours at 130°, cooled and filtered. The filtrate (in several portions) was treated with 500 ml of 2% aqueous NaOH. The thionaphthostyryl was isolated from the aqueous layer with hydrochloric acid. The yield was 1.84 g (67.2%) and the m.p. 152-157°. After recrystallization from benzene, the substance had m.p. 156.6-157.6°. It was identical with the substance obtained from 1-naphthyl isocyanate [5].

N-Methylnaphthostyryl [1-methylbenz-(c,d)-indolin-2-one]. 5.0 g of naphthostyryl was added to a solution of 12 g of NaOH in 50 ml of water. Over a period of two hours, 14 ml of dimethyl sulfate was added at 40-42°, the mixture was stirred for a further one hour and the product filtered and washed with water. The greasy precipitate was dissolved in ether, separated from the water and dried and the ether evaporated. The residue (about 5 ml) was cooled, filtered and the precipitate recrystallized from benzine. The yield of (III) was 1.65 g (30.4%) and the m.p. 77.0-79.2° (72-75° [6]).

Found %: C 78.47, 78.68; H 4.95, 4.81; N 7.41, 7.31. $C_{12}H_9ON$. Calculated %: C 78.68; H 4.91; N 7.65.

5.0 g of naphthostyryl and 9.0 g of K_2CO_3 in 25 ml of trichlorobenzene was heated to 150° and a mixture of 15 ml of methyl benzenesulfonate and 15 ml of trichlorobenzene added over a period of four hours. The mixture was filtered and the trichlorobenzene distilled from the filtrate, in steam. The residue was extracted with ether and dried and the ether distilled off completely. The yield of (III) was 1.7 g (31.3%). After recrystallization from 15 ml of benzine, the substance had m.p. 77.8-79.8°.

N-Methylthionaphthostyryl [1-methyl-2-thionebenz-(c,d)-indoline] (IV). 1.65 g of N-methylnaphthostyryl and 2.0 g of phosphorus pentasulfide in 30 ml of xylene were stirred at 130° for four hours. The reaction mixture was filtered, half the xylene distilled off from the filtrate, the precipitated tars separated and the xylene distilled off completely. The residue (1.1 g) melted at 90-120°. After two recrystallizations from alcohol, the yellow needles had m.p. 127.2-130.4°.

Found %: C 71.91, 71.81; H 4.47, 4.62; N 6.77, 6.84; S 16.04. $C_{12}H_9NS$. Calculated %: C 72.36; H 4.53; N 7.03; S 16.08.

We would like to thank D.N. Shigorin and E.S. Levin for the optical measurements.

SUMMARY

1. Treatment of naphthostyryl and N-methylnaphthostyryl with phosphorus pentasulfide gave thionaphthostyryl and N-methylthionaphthostyryl.

2. N-Methylnaphthostyryl was prepared by methylation of naphthostyryl.

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THE PREPARATION OF o-NITROSOPHENOL FROM SALICYLIC ACID

A.A. Nemodruk

o-Nitrosophenol is a valuable analytical reagent for the determination of copper [1-3], cobalt [4] and divalent iron [5]. The methods of determining the elements listed using o-nitrosophenol are distinguished by high selectivity and great sensitivity. For example, in determining Fe^{II} with o-nitrosophenol, the sensitivity is three times greater than the determination with α,α'-dipyridyl [5]. There are also reports of the successful use of o-nitrosophenol for determining mercury, nickel, palladium and zinc [5, 6].

The difficulty of its preparation is an obstacle to the wide use of o-nitrosophenol as an analytical reagent.

o-Nitrosophenol was first prepared by Baeyer and Knorr [7] from o-nitrosoanisole by hydrolyzing it with boiling $KHSO_4$ solution. Due to the low yield of o-nitrosophenol and the poor availability of the starting o-nitrosoanisole, a series of attempts was made to prepare o-nitrosophenol by other methods. In particular, preparations were put forward for o-nitrosophenol from the p-toluenesulfonic ester of o-nitrophenol [8] and then from o-nitroanisole [1] by treatment with amyl nitrite in an aqueous alcohol solution in the presence of ammonia and zinc dust. The o-methoxynitrosophenylhydroxylamine formed precipitated as a complex copper salt, which was treated with lime in boiling xylene and, after acidification of the mixture, the o-nitrosophenol formed was extracted with petroleum ether.

o-Nitrophenol was also proposed as a starting material for the preparation of o-nitrosophenol [2]. Later, a series of variations was proposed for the preparation of o-nitrosophenol directly from benzene [9-11] using copper acetate, potassium nitrite and hydrogen peroxide or ammonium pentacyanoferroate, hydroxylamine and hydrogen peroxide.

Although these methods differed from the preceding ones in great simplicity and ready availability of starting materials, as before, their fault was the insignificant yield of o-nitrosophenol.

A preparation for o-nitrosophenol is also described – by treatment of phenol with hydroxylamine hydrochloride in the presence of copper acetate and hydrogen peroxide [12]. The main reaction product in this case is p-nitrosophenol and only an insignificant amount of o-nitrosophenol is formed.

The author recently showed that when salicylic acid was treated with nitrous acid in an acetic acid medium, a nitroso group was introduced into the salicylic acid in place of the carboxyl group with the evolution of CO_2 and the formation of o-nitrosophenol, which then reacted with the nitrous acid to form o-diazophenol, the main reaction product [13]. Such a course of the reaction is explained by the fact that the stage of o-nitrosophenol formation is slower than the subsequent conversion to o-diazophenol. If the reaction is performed in the presence of copper salts, then the o-nitrosophenol immediately reacts with the Cu^{II} and is bound as a stable copper complex salt. In contrast to o-nitrosophenol itself, the complex shows no tendency for further reaction with nitrous acid.

In addition, o-nitrosophenol is not stable in aqueous solutions, while its complex copper salt has quite high stability. Due to this, almost all the o-nitrosophenol is accumulated in the reaction mixture as the complex copper salt. At the end of the reaction, the complex copper salt of o-nitrosophenol is decomposed with dilute hydrochloric acid and the free o-nitrosophenol extracted with petroleum ether. Saturation of the extract with ammonia gas precipitates the o-nitrosophenol as the ammonium salt. The o-nitrosophenol yield is about 65%. Up to 10% of 5-diazosalicylic acid (calculated on the original salicylic acid) was found among the reaction products. Thus, the nitrosation of the complex copper salt of salicylic acid is different from that of the complex aluminum, chromium and zinc salts of salicylic acid, described previously [14]. In comparison with these, the complex copper salt of salicylic acid has considerably less reactivity in nitrosation reactions. Nitrosation of the complex copper salt of salicylic acid is more similar to nitrosation of free salicylic acid. The difference is only that in this case, the o-nitrosophenol formed combines immediately with Cu^{II} in a stable complex compound, in which the nitroso group is shielded from further reaction with nitrous acid. On the other hand, in the complex copper salt of 5-nitrososalicylic acid formed, the nitroso group is not shielded from further reaction with nitrous acid and hence it is readily converted into the complex copper salt of 5-diazosalicylic acid. Since the complex copper salt of 5-nitrososalicylic acid is formed very slowly from the complex copper salt of salicylic acid and then its conversion into the complex copper salt of 5-diazosalicylic acid proceeds at a considerably greater rate, the content of complex copper salt of 5-nitrososalicylic acid of the reaction mixture does not exceed 2%, calculated on the original salicylic acid.

Papers stating that 5-nitrososalicylic acid is formed in 97% yield by treatment of the complex copper salt of salicylic acid with nitrous acid [15-17] are incorrect.

EXPERIMENTAL

Preparation of o-nitrosophenol. 4 g of sodium salicylate was dissolved in 50 ml of water and 5 g of $NaNO_2$ was added, followed by 10 g of copper sulfate, dissolved in 50 ml of water and 2.5 ml of glacial acetic acid. The yellow-green solution was heated to 50-55° and kept at this temperature for six hours. The solution color changed from yellow-green and became an intense red. At the same time a dark-red precipitate formed. The reaction mixture was kept at 20-25° for 12 hours. Then 20 ml of a 10% sulfamic acid solution was added to remove the unreacted nitrous acid. After 5-10 minutes, 50 ml of dilute (1: 1) hydrochloric acid was added to decompose the complex copper salt of o-nitrosophenol formed. The latter was extracted with petroleum ether (3 · 50 ml). The ether extract was washed twice with water to remove traces of hydrochloric acid. The solution of o-nitrosophenol obtained was quite pure and could be used directly for analytical purposes.

The solution of o-nitrosophenol in petroleum ether could be stored at room temperature without noticeable change for 3-4 days and at 0° for up to two weeks. The o-nitrosophenol itself could not be isolated in a large amount as it decomposed extremely rapidly, going partly to o-nitrophenol and partly to unknown products. In addition, due to its extremely high volatility, a considerable part of it was lost during the evaporation of the petroleum ether. After evaporation of a petroleum ether solution of o-nitrosophenol on a clock glass, light, greenish-yellow needle-like crystals of pure o-nitrosophenol were left and these had a characteristic sharp smell. To determine the o-nitrosophenol yield, the substance was extracted completely with petroleum ether (until there was no longer a positive reaction when 1% copper sulfate solution was added to 0.5-1 ml of extract). The whole extract was collected in a graduated flask of 250-ml capacity and made up to the mark with petroleum ether. 5 ml of 1 N NaOH solution was added to 10 ml of the organic solution, the mixture shaken thoroughly and the aqueous layer separated. The extraction was repeated with a fresh portion of NaOH. The o-nitrosophenol content of the aqueous solution obtained was determined by titration with vanadous sulfate [17]. The yield of o-nitrosophenol was 65%, calculated on the sodium salicylate.

By reaction with alkaline solutions of resorcinol and 1,8-aminonaphthol-3,6-disulfonic acid to form the azo dyes, it was established that the reaction mixture,after separation of the o-nitrosophenol, contained a diazo compound. The diazo compound was determined quantitatively by Hantzsch's method [18]. For this, the reaction mixture (after separation of the o-nitrosophenol) was transferred to a 250-ml graduated flask and diluted to the mark with water and 25 ml of this solution (solution A) was used for each determination. The amount of diazo compound found was 9.4% (calculated on the sodium salicylate).

When 50 ml of solution A (first neutralized with soda was treated with 0.8 g of resorcinol) dissolved in 10 ml of 10% soda solution, the azo dye formed was extracted with ethyl ether after acidification and then the ether extract obtained passed through a column filled with chromatographic grade aluminum oxide, two different azo compounds were obtained. One of these was identified by the light absorption curve in aqueous solutions as 2,2',4-trihydroxyazobenzene and the other as 2,4,4'-trihydroxyazobenzene-3'-carboxylic acid. The yields of these, determined by titration with VSO_4 solution [17], were 2.7 and 6.9%, respectively, calculated on the sodium salicylate.

A nitroso compound, which differed from o-nitrosophenol in that it was not extracted with petroleum ether, but was readily extracted with ethyl ether, was detected in solution A by a well-known, qualitative test [9]. It was isolated from the mixture by chromatography of the ether solution on aluminum oxide. The amount of it, determined according to [17], was 1.2% (calculated on the sodium salicylate). After reduction with zinc dust in hydrochloric acid, the amino compound formed was diazotized and coupled with resorcinol. The azo compound obtained was identified by the light absorption curve as 2,4,4'-trihydroxyazobenzene-3-carboxylic acid. Consequently, when the complex copper salt of salicylic acid was treated with nitrous acid under the conditions described, it yielded 65% of o-nitrosophenol, 2.7% of o-diazophenol, 9.6% of diazosalicylic acid and 1.2% of 5-nitrososalicylic acid, calculated on the salicylic acid.

Preparation of o-nitrosophenol ammonium salt. The solution of o-nitrosophenol in petroleum ether obtained was put into a dish and placed in a desiccator containing a small amount of concentrated ammonia solution. When the o-nitrosophenol had been converted into the ammonium salt completely (indicated by decolorization of the petroleum ether), the red precipitate of the ammonium salt of o-nitrosophenol was filtered off and washed with petroleum ether. The yield was 2.25 g.

Found %: C 51.30; H 5.70; N 19.85. $C_6H_8O_2N_2$. Calculated %: C 51.43; H 5.76; N 20.00

Preparation of complex copper salt of o-nitrosophenol. The complex copper salt of o-nitrosophenol was prepared as described above, with the difference that after the nitrosation reaction, the precipitate of the complex copper salt of o-nitrosophenol was not decomposed by the addition of hydrochloric acid, but was filtered off and washed with a small amount of cold water, then with alcohol and finally with ether. In comparison with o-nitrosophenol itself and its ammonium salt, the complex copper salt of o-nitrosophenol was considerably more stable. No signs of deterioration were detected when it was stored for 14 months. To prepare a solution in petroleum ether from it, it was treated with 4-6% hydrochloric acid and the liberated o-nitrosophenol extracted with petroleum ether.

A test was carried out for the formation of nitrososalicylic acid using Gulinov's method [15, 16], according to which 16 g of sodium salicylate was dissolved in 450 ml of water, a solution of 25-35 g of copper sulfate and 7 g of sodium nitrite in 150 ml of water added and the reaction mixture left for 9-10 days. The precipitate was filtered off and washed with a small amount of water, then with alcohol and ether. The precipitate was treated with 4-6% hydrochloric acid and then extracted with petroleum ether to isolate o-nitrosophenol. The latter was identified by analysis and the characteristic reaction colors with Fe^{II}, Co and Cu. By the method described above, the residue after separation of the o-nitrosophenol was shown to contain 1.9% of 5-nitrososalicylic acid, 5.4% of the 5-diazosalicylic acid and 0.7% of o-diazophenol (calculated on sodium salicylate).

SUMMARY

A method was developed for preparing o-nitrosophenol from salicylic acid by the action of sodium nitrite in acetic acid solution in the presence of cupric salts, which form a stable complex salt with o-nitrosophenol and shield it from further reaction with nitrous acid, which converts it to o-diazophenol.

The method described for the preparation of o-nitrosophenol differs from methods described up to now in its exceptional simplicity, the availability of the starting materials and the high yield.

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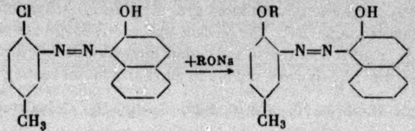
THE REPLACEMENT OF HALOGEN IN AZO COMPOUNDS

IV. THE REPLACEMENT OF CHLORINE IN 5-METHYL-2-CHLOROBENZENEAZO-2'-NAPHTHOL BY ALKOXY AND AROXY GROUPS AND THE PREPARATION OF ETHERS OF 3-AMINO-4-HYDROXYTOLUENE

B.I. Stepanov

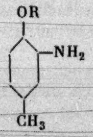
In extending the method of replacing the halogen in o-halo-o'-hydroxyazo dyes, which was tested on 2-chlorobenzeneazo-2'-naphthol [1-3], to other examples, we prepared a series of azo dyes – derivatives of ethers of 3-amino-4-hydroxytoluene – from 5-methyl-2-chlorobenzeneazo-2'-naphthol.



R=C_2H_5, n.-C_4H_9, $(CH_3)_2CHCH_2CH_2$, n.-C_6H_{13}, n.-C_8H_{17}, n.-$C_{18}H_{37}$, $C_6H_5CH_2$, $C_6H_5CH_2CH_2$, $C_6H_5CH_2CH_2CH_2$, C_6H_5, 3,5-$(CH_3)_2C_6H_3$, & 4-$(CH_3)_3CCH_2C(CH_3)_2C_6H_4$.

The reaction with the alcoholates was more convenient to perform in a mixture of the corresponding alcohol and with an inert solvent (toluene or xylene). In this case, the consumption of alcohol was reduced and the reaction product was more readily isolated and purified. The dyes with alkoxy and aroxy groups obtained were capable of coloring acetate and polyamide fibers.

Reductive cleavage of the dyes obtained gave a series of ethers of 3-amino-4-hydroxytoluene.



R=n-C_4H_9, $(CH_3)_2CHCH_2CH_2$, n-C_6H_{13}, n-C_8H_{17}, n.-$C_{18}H_{37}$, $C_6H_5CH_2CH_2$, $C_6H_5CH_2CH_2CH_2$, 3,5-$(CH_3)_2C_6H_3$.

EXPERIMENTAL

The starting azo dye was prepared by diazotizing 3-amino-4-chlorotoluene (m.p. 29-30°) and coupling the product with 2-naphthol. After recrystallization from toluene, the reddish-orange, lustrous needles had m.p. 163.5-164°. The dye was soluble in toluene, chlorobenzene and glacial acetic acid, less soluble in methyl and ethyl alcohols and insoluble in water. A solution in concentrated sulfuric acid had a crimson color, which became orange when the solution was diluted with water.

Found %: C 68.39, 68.58; H 4.44, 4.53; N 9.27, 9.35. $C_{17}H_{13}ON_2Cl$. Calculated %: C 68.80; H 4.38; N 9.52.

Replacement of chlorine by alkoxy groups.* 4 g of starting dye was triturated with 2 g of copper sulfate and a solution of sodium alcoholate, prepared from 1 g of metallic sodium and 20 ml of the appropriate alcohol: ethyl, n-butyl (b.p. 117°), isoamyl (2-methylbutanol-4, b.p. 132°), n-hexyl (b.p. 157°), n-octyl (b.p. 194-195°), benzyl (b.p. 204-206°), β-phenylethyl (b.p. 219-221° at 750 mm), and γ-phenylpropyl (b.p. 235-237°). The mixture obtained was diluted with 20 ml of toluene and heated and stirred for 10-12 hours at 100-110° (in the case of ethyl alcohol – heated on a water bath with a temperature of 74-75° inside the flask). In the case of n-octadecyl alcohol (m.p. 58.5°), the alcoholate was prepared by reacting 20 g of the alcohol with 1 g of metallic sodium at 150-160°, the solution of octadecylate cooled to 95° and a suspension of copper sulfate (2 g) in a solution of the starting dye (4 g) in toluene (20 ml) added to it.

After the heating, the toluene and the excess of the appropriate alcohol was distilled away in vacuum, the residue diluted with water and the residue filtered off (in the case of octadecyl alcohol the excess was removed by washing with hot methyl alcohol). The residue was then boiled with concentrated hydrochloric acid, the mass diluted with water, filtered, washed free from chloride ion and dried in air. A test for chlorine was negative.

We obtained 3.52 g (85.4%) of the ethoxy-substituted dye. After recrystallization from glacial acetic acid, the coarse needles had m.p. 184.5°. The dye was readily soluble in benzene, toluene, chloroform and carbon tetrachloride in the cold and in acetone and glacial acetic acid on heating; it was almost insoluble in methyl and ethyl alcohols in the cold, dissolved slightly in methyl alcohol on heating and slightly more in ethyl alcohol and was insoluble in water.

Found %: N 9.14. $C_{19}H_{18}O_2N_2$. Calculated %: N 9.15.

We obtained 4.4 g (97.7%) of the butoxy-substituted dye. After recrystallization from glacial acetic acid, the tufts of fine, lustrous needles had m.p. 139°. The product was readily soluble in benzene, toluene and chloroform in the cold and in acetone, glacial acetic acid and carbon tetrachloride on heating; it was difficultly soluble in methyl alcohol, even on heating, slightly more soluble in ethyl alcohol on heating and insoluble in water.

Found %: C 75.36, 75.23; H 6.61, 6.76; N 8.46, 8.26. $C_{21}H_{22}O_2N_2$. Calculated %: C 75.45; H 6.59; N 8.38.

We obtained 3.82 g (81.5%) of the 3-methylbutoxy-substituted dye. After recrystallization from acetone, the long needles had m.p. 142.5°. The material was readily soluble in benzene, toluene, chloroform and carbon tetrachloride in the cold, less soluble in acetone, dissolved in methyl and ethyl alcohols on heating and was insoluble in water.

Found %: C 75.43, 75.55; H 7.38, 7.31; N 7.86, 7.98. $C_{22}H_{24}O_2N_2$. Calculated %: C 75.86; H 6.89; N 8.05.

3.1 g (63.5%) of the hexoxy-substituted dye was obtained. After recrystallization from glacial acetic acid, the lustrous needles had m.p. 110°. The product was readily soluble in benzene, toluene, chlorobenzene, chloroform and carbon tetrachloride in the cold and in methyl and ethyl alcohols, glacial acetic acid and acetone on heating; it was insoluble in water.

Found %: C 76.47, 76.33; H 7.41, 7.59; N 7.80, 7.61. $C_{23}H_{26}O_2N_2$. Calculated %: C 76.22; H 7.18; N 7.73.

3.77 g (71.6%) of the octoxy-substituted dye was obtained. After recrystallization from ethyl alcohol, the overgrown needles had m.p. 114°. The product was readily soluble in benzene, toluene and chloroform in the cold and in methyl and ethyl alcohols, acetone and carbon tetrachloride on heating; it was insoluble in water.

Found %: C 77.10, 77.20; H 7.76, 7.89; N 7.38, 7.32. $C_{25}H_{30}O_2N_2$. Calculated %: C 76.92; H 7.69; N 7.18.

4.68 g (65.1%) of the octadecoxy-substituted dye was obtained. After recrystallization from ethyl alcohol, the fine needles had m.p. 82°. The product was readily soluble in benzene, toluene, acetone, chloroform and carbon tetrachloride in the cold, in glacial acetic acid on heating and slightly less in methyl and ethyl alcohols; it was insoluble in water.

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*With the participation of I.B. Iurkov.

Found %: C 79.06, 79.13; H 9.39, 9.49; N 5.48. $C_{35}H_{50}O_2N_2$. Calculated %: C 79.24; H 9.43; N 5.28.

3.17 g (63.9%) of the phenylmethoxy-substituted dye was obtained. After recrystallization from acetone, the long needles had m.p. 175°. The product was readily soluble in benzene, toluene and chloroform in the cold and less soluble in acetone, but readily so on heating, and less so in methyl and ethyl alcohols and carbon tetrachloride; it was insoluble in water.

Found %: C 77.99, 78.11; H 5.54, 5.68; N 7.77, 7.71. $C_{24}H_{20}O_2N_2$. Calculated %: C 78.26; H 5.43; N 7.61.

4.11 g (79.8%) of the β-phenylethoxy-substituted dye was obtained. After recrystallization from glacial acetic acid, the needles had m.p. 169.5-170°. The substance was soluble in benzene, toluene, chlorobenzene, chloroform and carbon tetrachloride in the cold and on heating it dissolved readily in acetone and glacial acetic acid and sparingly in methyl and ethyl alcohols; it was insoluble in water.

Found %: C 78.34, 78.26; H 6.02, 5.99; N 7.53. $C_{25}H_{22}O_2N_2$. Calculated %: C 78.53; H 5.76; N 7.33.

4.1 g (76.7%) of the γ-phenylpropoxy-substituted dye was obtained. After recrystallization from ethyl alcohol, the fine needles had m.p. 138°.

Found %: C 78.99, 78.80; H 6.22, 6.12; N 7.26, 7.07. $C_{26}H_{24}O_2N_2$. Calculated %: C 78.78; H 6.06; N 7.07.

Replacement of chlorine by the phenoxy group.* 4 g of the starting dye, ground up with 2 g of copper sulfate, was added to a solution of phenolate prepared by reacting 20 g of phenol with 30 ml of 30% sodium hydroxide solution, and the mixture heated under reflux with stirring for ten hours at 110°. The reaction mixture was then filtered and the precipitate washed, first with 5% sodium hydroxide solution to remove excess phenol and then with water, and boiled with 70 ml of concentrated hydrochloric acid. The mixture was diluted with water and the dye filtered off, washed free from ionic chlorine and dried at 70°. The weight was 4.1 g (85.9%). A test for chlorine was negative. After recrystallization from acetone, the flat needles had m.p. 169.5-170°. A mixture with the starting dye (m.p. 163.5-164°) had a depressed melting point (to 140-146°). In the cold, the phenoxy-substituted dye was readily soluble in benzene, toluene, chlorobenzene, chloroform and carbon tetrachloride and poorly so in methyl and ethyl alcohols and acetone; on heating, it dissolved slightly more in methyl and ethyl alcohols and readily in acetone; it was insoluble in water.

Found %: C 77.62, 77.75; H 5.89, 6.03; N 7.61. $C_{23}H_{18}O_2N_2$. Calculated %: C 77.96; H 5.08; N 7.91.

Replacement of chlorine by the 3,5-dimethylphenoxy group. 4 g of the starting dye, ground with 2 g of copper sulfate, was added to a solution of xylenolate, prepared by reacting 5 g of 1,3,5-xylenol with 11 g of 16.5% sodium hydroxide solution and the mixture heated under reflux with stirring for ten hours at 105-110°. The reaction mixture was diluted with water, and the precipitate filtered off, washed free from excess xylenol with 5% sodium hydroxide solution and then water and boiled with 50 ml of concentrated hydrochloric acid. The mixture was diluted with water and the dye filtered off, washed free from ionic chlorine and dried in air. The weight was 4.75 g (92.6%). A test for chlorine was negative. After recrystallization from glacial acetic acid, the flat needles had m.p. 163.5-164°. A mixture with the starting dye (m.p. 163.5-164°) had a depressed melting point (to 139°). The 3,5-dimethylphenoxy-substituted dye was readily soluble in benzene, toluene, acetone, chloroform and carbon tetrachloride and slightly less so in glacial acetic acid; it dissolved sparingly in ethyl alcohol in the cold, but readily on heating, was insoluble in methyl alcohol in the cold and dissolved sparingly on heating and did not dissolve in water.

Found %: C 78.57, 78.45; H 5.90, 5.99; N 7.46. $C_{25}H_{22}O_2N_2$. Calculated %: C 78.53; H 5.76; N 7.33.

Replacement of chlorine by the 4-(1',1',3',3'-tetramethylbutyl)-phenoxy group (p-isooctylphenoxy group). 3 g of the starting dye, ground with 1.5 g of copper sulfate, was added to a mixture of isooctylphenolate and xylene, prepared by reacting 7 g of 4-isooctylphenol with 0.7 g of metallic sodium in 30 ml of xylene with heating. The mixture formed was heated under reflux with stirring for 16 hours at 105-110° and then the xylene distilled off in vacuum at 90°. The residue was boiled several times with 5% sodium hydroxide solution to remove the excess isooctylphenol, washed with water and boiled with 50 ml of concentrated hydrochloric acid. The mixture was diluted with water and the dye filtered off, washed free from ionic chlorine and dried at 80°. The weight was 4.65 g (98.7%). A test for chlorine was negative. After recrystallization from glacial acetic acid, the bunches of fine needles had m.p. 171-172°. The isooctylphenoxy-substituted dye was readily soluble in benzene, toluene, chloroform, carbon tetrachloride and acetone in the cold, and in glacial acetic acid and ethyl alcohol on heating; it was sparingly soluble in methyl alcohol and insoluble in water.

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*V.S. Zenkevich participated in the experiments with phenolates.

Found %: C 79.63, 79.57; H 7.38, 7.48; N 6.18. $C_{31}H_{34}O_2N_2$. Calculated %: C 79.82; H 7.29; N 6.00.

Preparation of ethers of 3-amino-4-hydroxytoluene. 2 g of the appropriate alkoxy or aroxy substituted azo dye (see above) was reduced by boiling with a solution of stannous chloride (prepared by reacting 3 g of metallic tin with 30 ml of concentrated hydrochloric acid with heating and by diluting with 30 ml of water before introducing the dye) under reflux until it was decolorized. The following day, the inhomogeneous precipitate, which formed overnight, was filtered off and treated with 50 ml of 5% sodium hydroxide solution, containing 0.75 g of sodium hydrosulfite, and then the 3-amino-4-alkoxy-(or aroxy)-toluene extracted several times with ether (a total volume of about 50 ml). The ether layer was separated and treated with 1 ml of concentrated hydrochloric acid and the precipitate of the amine hydrochloride filtered off, dried in air and purified by recrystallization.

To prepare the N-benzoyl derivatives, 0.1 g of the amine hydrochloride was treated with 2 ml of 20% sodium hydroxide solution and 0.5 ml of benzoyl chloride. The benzoyl derivative was washed with water, triply diluted hydrochloric acid and again with water, dried in air and recrystallized from methyl alcohol.

1.14 g (88.4%) of 3-amino-4-butoxytoluene hydrochloride was obtained. After recrystallization from water acidified with several drops of hydrochloric acid, the fine needles had m.p. 169°.

The N-benzoyl derivative of 3-amino-4-butoxytoluene formed long needles with m.p. 67°.

Found %: C 76.23, 76.18; H 7.73, 7.64; N 4.68, 4.58. $C_{18}H_{21}O_2N$. Calculated %: C 76.32; H 7.42; N 4.94.

1.23 g (93.1%) of 3-amino-4-(3'-methylbutoxy)-toluene hydrochloride was obtained. After recrystallization from water, acidified with several drops of hydrochloric acid (with preliminary decoloration of the solution with activated charcoal), the fine, branched filaments had m.p. 168°.

The N-benzoyl derivative of 3-amino-4-(3'-methylbutoxy)-toluene formed fine needles with m.p. 72°.

Found %: N 4.60, 4.51; $C_{19}H_{23}O_2N$. Calculated %: N 4.71.

1.2 g (96%) of 3-amino-4-hexoxytoluene hydrochloride was obtained. After recrystallization from water acidified with several drops of hydrochloric acid, the long needles melted at 171°.

Found %: C 63.93, 63.86; H 9.30, 9.40; N 5.83, 5.90. $C_{13}H_{22}ONCl$. Calculated %: C 64.06; H 9.03; N 5.77.

The N-benzoyl derivative of 3-amino-4-hexoxytoluene formed long needles with m.p. 73°.

Found %: C 76.59, 76.45; H 8.19, 8.22; N 4.33, 4.25. $C_{20}H_{25}O_2N$. Calculated %: C 77.17; H 8.04; N 4.50.

1.13 g (89.3%) of 3-amino-4-octoxytoluene hydrochloride was obtained. After recrystallization from dilute hydrochloric acid with a small amount of methyl alcohol added, the long needles had m.p. 125-125.5°.

Found %: C 66.64, 66.50; H 9.57, 9.74; N 4.92, 5.00. $C_{15}H_{22}ONCl$. Calculated %: C 66.29; H 9.57; N 5.15.

0.74 g (47.7%) of 3-amino-4-octadecoxytoluene hydrochloride was obtained. After recrystallization from dilute methyl alcohol acidified with several drops of hydrochloric acid, the fine needles had m.p. 119-120°.

Found %: C 72.87, 73.02; H 11.65, 11.40; N 3.97, 3.81. $C_{25}H_{46}ONCl$. Calculated %: C 72.90; H 11.18; N 3.40.

The N-benzoyl derivative of 3-amino-4-octadecoxytoluene formed fine, flat needles with m.p. 61°.

Found %: C 79.86, 79.99; H 10.64, 10.72; N 2.85, 2.83. $C_{32}H_{49}O_2N$. Calculated %: C 80.16; H 10.23; N 2.92.

1.27 g (91.8%) of 3-amino-4-(β-phenylethoxy)-toluene hydrochloride was obtained. After recrystallization from dilute methyl alcohol, the balls of fine needles had m.p. 167-177° (with decomp.) and 187-188.5° (in a sealed capillary).

Found %: C 68.87, 68.78; H 6.85, 6.90; N 5.84, 5.92. $C_{15}H_{18}ONCl$. Calculated %: C 68.31; H 6.83; N 5.31.

The N-benzoyl derivative of 3-amino-4-(β-phenylethoxy)-toluene formed long lustrous flat needles with m.p. 92.5-93°.

Found %: C 79.86, 79.73; H 6.44, 6.56; N 4.51, 4.62. $C_{22}H_{21}O_2N$. Calculated %: C 79.76; H 6.34; N 4.23.

1.04 g (74.3%) of 3-amino-4-(γ-phenylpropoxy)-toluene hydrochloride was obtained. After recrystallization from dilute methyl alcohol acidified with several drops of hydrochloric acid, the fine, branched needles had m.p. 159-160°.

The N-benzoyl derivative of 3-amino-4-(γ-phenylpropoxy)-toluene formed long, flat needles with m.p. 85-85.5°.

Found %: C 80.25, 80.32; H 6.66, 6.86. $C_{23}H_{23}O_2N$. Calculated %: C 80.00; H 6.67.

1.3 g (94.6%) of 3-amino-4-(3',5'-dimethylphenoxy)-toluene hydrochloride was obtained. After recrystallization from methyl alcohol acidified with several drops of hydrochloric acid, the long, flat needles had m.p. 163-163.5°.

Found %: C 68.11, 67.97; H 7.00, 7.20. $C_{15}H_{18}ONCl$. Calculated %: C 68.31; H 6.83.

The N-benzoyl derivative of 3-amino-4-(3',5'-dimethylphenoxy)-toluene formed fine needles with m.p. 146.5-146.7°.

SUMMARY

1. On reacting sodium alcoholates and phenolates with the azo dye from 3-amino-4-chlorotoluene and 2-naphthol in the presence of a copper salt, the chlorine atom was replaced by the alkoxy and aroxy groups with ethyl, n-butyl, isoamyl (3-methylbutyl), n-hexyl, n-octyl, n-octadecyl, benzyl, β-phenylethyl, γ-phenylpropyl, phenyl, 3,5-dimethylphenyl and 4-(1',1',3',3'-tetramethylbutyl)-phenyl (p-isooctylphenyl) residues.

2. It was found that the reaction of the halogen-containing dye and the alcoholate could be performed more conveniently in a mixture of the appropriate alcohol and an inert solvent (toluene or xylene).

3. Reductive cleavage of the alkoxy and aroxy substituted dyes gave ethers of 3-amino-4-hydroxytoluene with n-butyl, isoamyl (3-methylbutyl), n-hexyl, n-octyl, n-octadecyl, β-phenylethyl, γ-phenylpropyl and 3,5-dimethylphenyl residues in the ether group.

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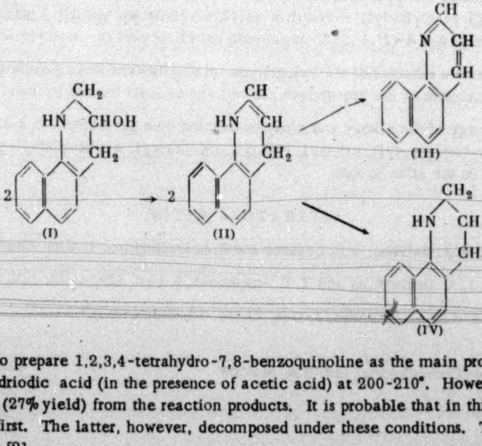
INVESTIGATION OF THE PRODUCTS FROM THE REACTION OF EPICHLOROHYDRIN AND AROMATIC AMINES

III. THE ACTION OF HYDROCHLORIC ACID AND THIONYL CHLORIDE ON 3-HYDROXY-1,2,3,4-TETRAHYDRO-7,8-BENZOQUINOLINE AND ON 3-HYDROXY-1,2,3,4-TETRAHYDRO-5,6-BENZOQUINOLINE

N.N. Vorozhtsov, Jr. and S.I. Kutkevichus

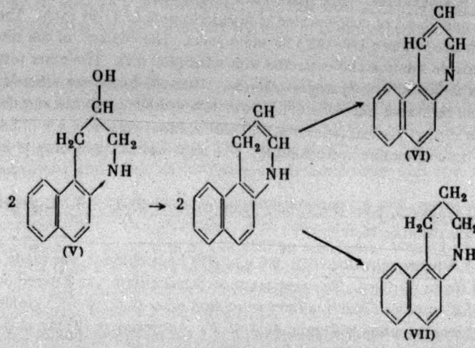
We undertook an investigation of the action of hydrochloric acid and thionyl chloride on 3-hydroxy-1,2,3,4-tetrahydro-7,8-benzoquinoline (I) (see [1] for preparation), so as to replace the hydroxyl group by a chlorine atom. However, the action of these reagents on (I) did not lead to the required result. When (I) was heated (to 170-200°) with hydrochloric acid under pressure, we obtained a mixture of two bases, which did not contain halogen, and one of them was 7,8-benzoquinoline (III) (42-44% yield) and the other its 1,2,3,4-tetrahydro derivative (IV) (27 to 33%).

Apparently, this conversion began with the elimination of a molecule of water to form the 1,2- or 1,4-dihydro derivative of benzoquinoline (II), which then disproportionated into benzoquinoline (III) and its tetrahydro derivative (IV).



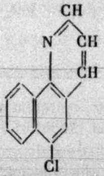
We attempted to prepare 1,2,3,4-tetrahydro-7,8-benzoquinoline as the main product by reduction of (I) by heating it with hydriodic acid (in the presence of acetic acid) at 200-210°. However, we were only able to isolate substance (III) (27% yield) from the reaction products. It is probable that in this case a mixture of (III) and (IV) was formed first. The latter, however, decomposed under these conditions. The instability of (IV) has been noted previously [2].

Conversion into the corresponding quinoline and its tetrahydro derivative under the action of hydrochloric acid is not peculiar to (I) only, but apparently is characteristic of 3-hydroxy-1,2,3,4-tetrahydro derivatives of quinoline in general. Thus, under the same conditions, 3-hydroxy-1,2,3,4-tetrahydro-5,6-benzoquinoline (V) also gave approximately equal amounts of 5,6-benzoquinoline (VI) and 1,2,3,4-tetrahydro-5,6-benzoquinoline (VII).



The formation of a mixture of a quinaldine derivative and its 1,2,3,4-tetrahydro compound was noted previously when boiling together hydrochloric acid and the so-called aldol bases – compounds represented by the structure of 4-hydroxy-2-methyl-1,2,3,4-tetrahydroquinolines [3]. Consequently, both 3- and 4-hydroxy derivatives of 1,2,3,4-tetrahydroquinolines are capable of being converted into a mixture of the quinoline and its tetrahydro derivative. With the 3-hydroxy derivatives, considerably more drastic conditions are required than with the 4-hydroxy derivatives.

Somewhat unexpected results were obtained when 3-hydroxy-1,2,3,4-tetrahydro derivatives of benzoquinolines were treated with thionyl chloride. Thus, when (I) was heated with thionyl chloride for three hours on a boiling water bath, the reaction product isolated was a base with m.p. 100.7-101.0°, containing chlorine and with the composition of $C_{13}H_8NCl$. When treated with picric acid it gave a picrate with m.p. 243.2-243.7°. 6-Chloro-7,8-benzoquinoline (VIII) has the same composition and melting point and is obtained by heating 1-nitronaphthalene with glycerol and hydrochloric acid in a sealed tube [4]. We repeated the synthesis of the Polish investigators (whose data we can confirm completely) and established that mixed melting points of our compound with 6-chloro-7,8-benzoquinoline,



(VIII)

and also the corresponding picrates, were not depressed.

The yield of 6-chloro-7,8-benzoquinoline from the action of thionyl chloride on (I) was about 50%. It is noteworthy that substance (VIII) was isolated directly from the reaction mixture in quite a pure state – the melting point was only about 1-1.5° lower than that of the pure substance.

3-Hydroxy-1,2,3,4-tetrahydro-5,6-benzoquinoline (V) was treated with thionyl chloride under the same conditions to form 5,6-benzoquinoline (VI) in 65-68% yield.

We hope to examine the mechanism of the reaction between 3-hydroxy-1,2,3,4-tetrahydroquinoline derivatives and thionyl chloride in one of our next communications.

EXPERIMENTAL

Reaction of 3-hydroxy-1,2,3,4-tetrahydro-7,8-benzoquinoline (I) with hydrochloric acid. 1,2,3,4-Tetrahydro-7,8-benzoquinoline hydrochloride. Nine glass tubes were loaded with 1.0 g of 3-hydroxy-1,2,3,4-tetrahydro-7,8-benzoquinoline and 25 ml of concentrated hydrochloric acid (d.1.19) each. The sealed tubes were heated on an oil bath (bath temperature 190-195°) for eight hours. The contents of the tubes were made alkaline with 25% sodium hydroxide solution and extracted with ether (400 ml). The ether solution was dried with sodium carbonate and then saturated with hydrogen chloride. After two hours, the ether layer was poured off, the hydrochloride which had separated treated with 35 ml of 15% hydrochloric acid and the precipitate filtered off. Recrystallization from methyl alcohol (with charcoal purification) yielded 1.4 g (12.4%) of rhombic crystals of 1,2,3,4-tetrahydro-7,8-benzoquinoline hydrochloride. The m.p. was 262° (decomp.); according to [2], the m.p. is 260-261°.

Found %: C 71.2, 71.2; H 6.6, 6.5; N 6.1, 6.3; ionic chlorine 16.0, 16.1. $C_{13}H_{13}N \cdot HCl$. Calculated %: C 71.1; H 6.4; N 6.4; ionic chlorine 16.1.

1,2,3,4-Tetrahydro-7,8-benzoquinoline (IV). 0.6 g of (IV) hydrochloride was made alkaline with 6 ml of 10% sodium hydroxide and steam distilled. The precipitate in the distillate was filtered off. The weight was 0.3 g and the m.p. 44.1-44.8°. Recrystallization from petroleum ether (b.p. 45-65°) yielded colorless crystals of 1,2,3,4-tetrahydro-7,8-benzoquinoline with m.p. 45.4-45.9°. According to [2] the m.p. is 46.5°.

The picrate of 1,2,3,4-tetrahydro-7,8-benzoquinoline was prepared by mixing alcohol solutions of 0.10 g of (IV) and 0.13 g of picric acid (volume after mixing, 8 ml). The precipitate was collected. The yellow needles had m.p. 154.0-155.0° (from methyl alcohol).

Found %: N 13.5, 13.4. $C_{19}H_{16}O_7N_4$. Calculated %: N 13.6.

N-benzoyl-1,2,3,4-tetrahydro-7,8-benzoquinoline. The filtrate after separation of the precipitate of 1,2,3,4-tetrahydro-7,8-benzoquinoline hydrochloride (see above) and the residue, obtained by evaporating the mother liquors from recrystallization of this substance, were combined, made alkaline with 25% sodium hydroxide solution and extracted with ether (400 ml). The ether was distilled off, the residue (5.8 g) dissolved in 30 ml of ether and treated with 2.3 g of finely powdered potassium carbonate and 3.4 g of benzoyl chloride added dropwise over a period of 30 minutes, while the mixture was heated on a water bath (50-60°). After three hours heating, the reaction mixture was shaken with 25 ml of 10% sodium hydroxide. The precipitate was filtered off and washed with ether and water. The weight was 1.3 g; a further 0.4 g was isolated from the filtrate (ether layer) after extracting the 7,8-benzoquinoline from it with hydrochloric acid. The yield was 13% and the m.p. 188-189.5°. Recrystallization from methyl alcohol (with charcoal purification) yielded 1.3 g of colorless, crystalline needles of N-benzoyl-1,2,3,4-tetrahydro-7,8-benzoquinoline with m.p. 191.5-192.0°.

Found %: N 4.8, 4.9. $C_{20}H_{17}ON$. Calculated %: N 4.9.

A mixed melting point with a preparation, obtained analogously from authentic (IV), was not depressed.

7,8-Benzoquinoline (III). The filtrate after separation of the N-benzoyl-1,2,3,4-tetrahydro-7,8-benzoquinoline was poured into a separating funnel and 150 ml of 3.3% hydrochloric acid and 75 ml of ether added to it. After separation of the aqueous layer, the ether solution was repeatedly (three times) extracted with hydrochloric acid (until there was no longer turbidity when the acid solution was made alkaline). The combined hydrochloric acid solutions were made alkaline with 20% sodium hydroxide and extracted with ether. After removal of the ether, the 7,8-benzoquinoline was steam distilled. The weight was 3.5 g (44.4%) and the m.p. 49.7-50.3°. Recrystallization from petroleum ether gave colorless crystals of (III) with m.p. 50.5-51.0°. The literature reports 50.0° [5] and 52.0° [6].

Found %: C 87.2, 87.3; H 5.1, 5.0. $C_{13}H_9N$. Calculated %: C 87.1; H 5.1.

From substance (III) was prepared a hydrochloride with m.p. 214° (decomp.) and a picrate with m.p. 192.7-193.7°. The literature reports m.p. 213° [10] for the hydrochloride and 191.0-192.0° [6] for the picrate.

When the reaction was repeated with 9 g of (I) with hydrochloric acid under the same conditions, but isolating the whole of (IV) as the N-benzoyl derivative, the yield of this compound was 4.3 g (33%); 3.4 g (42%) of substance (III) was obtained.

The same yields were obtained when the reaction was performed with hydrochloric acid for 16 hours at 170-175°.

(III) was also obtained when (I) was reacted with hydriodic acid in the presence of acetic acid. Seven glass tubes were each loaded with 1.0 g of substance (I), 5 ml of acetic anhydride and 20 ml of concentrated hydriodic acid (d.1.55).

The tubes were heated on an oil bath at 200-210° for nine hours. The tubes were opened and the precipitate collected. The filtrate was made alkaline and extracted with ether to yield an insignificant amount of material, which was added to the precipitate and, after being made alkaline with 30% sodium hydroxide solution, steam distilled. The oily substance crystallized. The weight of (III) was 1.7 g and the m.p. 46.1-46.8°. Recrystallization from petroleum ether (b.p. 45-65°) gave a colorless product with m.p. 50-50.5°.

Reaction of 3-hydroxy-1,2,3,4-tetrahydro-5,6-benzoquinoline (V) with hydrochloric acid. N-Nitroso-1,2,3,4-tetrahydro-5,6-benzoquinoline. Two glass tubes, each containing 1.0 g of (V) and 25 ml of concentrated hydrochloric acid, were heated on an oil bath at 200-210° for nine hours. When the tubes had been opened, the contents were poured into a flask and made alkaline with 40% sodium hydroxide solution. The precipitate was collected, transferred to a flask, made alkaline with 3% sodium hydroxide and steam distilled. The oily substance crystallized. The weight was 1.0 g and the m.p. 90.5-91.5°. The crystalline substance was dissolved in 2% hydrochloric acid and sodium nitrite (as a 0.1 N solution) added to the solution until there was a reaction with starch-iodide paper. The N-nitroso-1,2,3,4-tetrahydro-5,6-benzoquinone was filtered off. The weight was 0.4 g and the m.p. 100.7-101.4°. Recrystallization from ether gave colorless plates with m.p. 104.8-105.1°. According to data in [7], the m.p. is 105.5°.

Found %: N 13.0, 13.2. $C_{13}H_{12}ON_2$. Calculated %: N 13.2.

5,6-Benzoquinoline (VI). The filtrate after separation of the N-nitroso-1,2,3,4-tetrahydro-5,6-benzoquinoline was made alkaline with 10% sodium hydroxide solution and the (VI) filtered off. The weight was 0.3 g and the m.p. 90.5-91.0°. According to data in [8], the m.p. is 93.5°.

Found %: C 87.0, 86.9; H 5.2, 5.1. $C_{13}H_9N$. Calculated %: C 87.1; H 5.1.

A picrate with m.p. 258.1-259.0° was also prepared. According to data in [9], the m.p. is 259°.

Reactions of (I) and (V) with thionyl chloride. 6-Chloro-7,8-benzoquinoline (VIII). 4.0 g of (I) and 20 ml of thionyl chloride were heated on a boiling water bath for three hours in a flask with a ground-glass jointed reflux condenser. When the reaction mixture had been cooled to room temperature, the precipitate was filtered off and dissolved in methyl alcohol and to the solution was added 25% sodium hydroxide in water until there was an alkaline reaction, and then 100 ml of water. Substance (VIII) was filtered off. The weight was 2.1 g and the m.p. 99.7-100.3°.

Recrystallization from methyl alcohol gave white needles of (VIII) with m.p. 100.7-101.0°. According to data in [4], the m.p. is 101°.

Found %: N 6.7, 6.6. $C_{13}H_8NCl$. Calculated %: N 6.6.

Hydrochloride of (VIII). 0.8 g of (VIII) was dissolved in 6 ml of methyl alcohol and the alcohol saturated with HCl. The hydrochloride of (VIII) was filtered off. The weight was 0.5 g and the m.p. 235° (decomp.). Recrystallization from methyl alcohol gave white needles of 6-chloro-7,8-benzoquinoline with m.p. 238° (decomp.).

Found %: N 5.7, 5.7; ionic chlorine 14.0, 14.1. $C_{13}H_8NCl \cdot HCl$. Calculated %: N 5.6; ionic chlorine 14.2.

A picrate of (VIII) with m.p. 243.5-244.0° was also prepared. According to data in [4], the m.p. is 240°.

Found %: C 51.6, 51.7; H 2.4, 2.3. $C_{19}H_{11}O_7N_4Cl$. Calculated %: C 51.5; H 2.6.

2.0 g of (V) and 8 ml of thionyl chloride were heated on a boiling water bath for 2.5 hours in a flask with a ground-glass jointed reflux condenser. The excess thionyl chloride was distilled off and the residue dissolved in 30 ml of methyl alcohol and heated for 15 minutes on a boiling water bath with activated charcoal. Then the hot filtrate was made alkaline with 10% sodium hydroxide in water and diluted with 100 ml of water. The 5,6-benzoquinoline, which precipitated over six hours, was collected. The weight was 1.2 g and the m.p. 85.1-86.5°.

Recrystallization from a mixture (15 : 1) of petroleum ether and methyl alcohol (using activated charcoal) gave white crystalline plates of (VI) with m.p. 90.2-90.7°.

SUMMARY

1. When 3-hydroxy-1,2,3,4-tetrahydrobenzoquinolines were heated with concentrated hydrochloric acid, mixtures of the corresponding benzoquinolines and tetrahydrobenzoquinolines were formed. The formation of these products may be explained by disproportionation of 1,2-(or 1,4-)dihydrobenzoquinolines, obtained as intermediates.

2. When 3-hydroxy-1,2,3,4-tetrahydro-7,8-benzoquinoline was treated with thionyl chloride, 6-chloro-7,8-benzoquinoline was obtained. When treated similarly, 3-hydroxy-1,2,3,4-tetrahydro-5,6-benzoquinoline gave 5,6-benzoquinoline. In the action of thionyl chloride on these compounds there occurred dehydration and dehydrogenation and in the case of 3-hydroxy-1,2,3,4-tetrahydro-7,8-benzoquinoline, chlorination of the aromatic nucleus as well.

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THE PROCESS OF POLYAMIDE RESIN FORMATION

VII. THE COMPOSITION AND STRUCTURE OF SALTS FORMED BY DICARBOXYLIC ACIDS AND DIAMINES OR HYDRAZINE

A.S. Shpital'nyi and Ia.A. Kharit

In work published previously [1], it was established that although the salts of dicarboxylic acids and aliphatic diamines could be either acidic or neutral, their composition was constant and did not depend on the ratio of the reacting components. The composition of the salt was determined by the relation of the dissociation constants of the acid. When the ratio had low values, neutral salts were formed and at high values, acid salts. These conclusions were arrived at as a result of studying the salts of adipic, succinic and oxalic acids.

In the present work the number of acids used for preparing the salts which interested us was increased to include azelaic and sebacic acids.

There are no diamines in the aliphatic series which possess strongly differing dissociation constants,as is observed among the acids [1]. To elucidate the effect on the salt composition of a high value of the ratio K_1/K_2 for the basic component, we used the dicarboxylic acid salts of hydrazine, which is known to have a very considerable value for K_1/K_2.

As previously [1], hexamethylenediamine and ethylenediamine were used as bases for salt formation. The preliminarily dissolved starting reagents were mixed, not only in equimolecular proportions, but also with a considerable excess of one or another of them. In only one case, actually in the preparation of a salt from hexamethylenediamine and excess sebacic acid, did we have to limit the excess of the acid due to difficulties in purifying the salt. In the rest of the experiments, no such limitations were required. A salt was also prepared from hexamethylenediamine and excess adipic acid,as the salt from these components, in the ratio of 1 : 2, was not examined in the previous work. K_1 and K_2 of azelaic and sebacic acids differ very insignificantly (Table 1).

TABLE 1

Name of acid	Dissociation constants
Sebacic	$K_1 = 2.34 \cdot 10^{-5}$ [2] $K_2 = 2.80 \cdot 10^{-5}$ [3] $K_2 = 2.55 \cdot 10^{-6}$ [4]
Azelaic	$K_1 = 2.88 \cdot 10^{-5}$ [5] $K_2 = 2.80 \cdot 10^{-6}$ [5]

Note: Temperature 25°.

Therefore, in accordance with the proposition above, one would expect that these acids would form salts of constant composition with diamines and the components of these would be present in equimolecular proportions. Judging by the data in Table 2, one would expect that neutral salts would crystallize at any ratio of the components. It was suggested that these salts should be represented as rings [1]

$$\begin{gathered}{}^{-}OOCRCOO^{-}\\ {}^{+}H_3NR_1NH_3^{+}\ .\end{gathered}$$

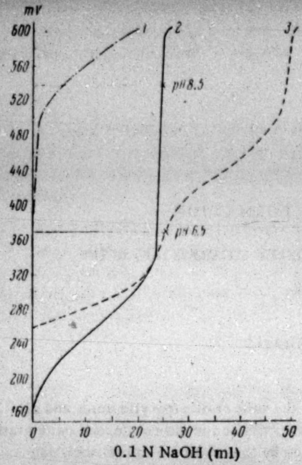
This type of representation has found support in handbooks on synthetic fibers with [6] and without [7] references to our work.

Apart from the considerations presented [1], evidence in favor of the cyclic structure is provided by a number of factors, for example, the capacity of related salts of ε-aminocaproic acid to form considerable amounts of rings (lactam) when distilled [8] or the presence in glycine crystals of hydrogen bonds between molecules lying in adjacent layers and not only in a linear direction [9], etc.

In contrast to diamines, the dissociation constants of hydrazine differ sharply from each other: at 25°, $K_1 = 8.5 \cdot 10^{-7}$ and $K_2 \approx 10^{-16}$ [10]. Due to the low value of the second dissociation constant, it is considered [11] that hydrazine is practically a monoacidic base and is more similar to ammonia and amines than to diamines. Although with dibasic mineral acids it is able to form salts of the type

$$(N_2H_4)_2H_2B,\ N_2H_4H_2B \text{ and } N_2H_42H_2B\ .$$

(H_2B is a dibasic acid), $N_2H_6^{++}$ ions do not exist in aqueous solution as they immediately react with water and are converted to $N_2H_5^+$. Therefore, a solution of hydrazine dihydrochloride is the same as a solution containing equimolecular amounts of free hydrogen chloride and hydrazine monochloride [11]. Raman spectra of crystals of divalent hydrazine show bands corresponding not only to divalent, but also to monovalent hydrazine ions ($N_2H_5^+$) [12].



Titration curves: 1) 0.05 M solution of 66 salt (hexamethylenediamine + adipic acid) (25 ml); 2) 0.025 M solution of adipic acid (50 ml); 3) 0.025 M solution of salt, obtained from hydrazine and adipic acid (50 ml).

According to our information, the description of salts of hydrazine and saturated dicarboxylic acids in the literature is limited to salts of oxalic [13] and succinic acids [14].

Since the aim of our investigations was to elucidate the effect of different ratios of starting components on the composition of the salt, we isolated a series of salts of hydrazine and dicarboxylic acids by the methods indicated above, including the salts that had been prepared previously.

From the data presented in Table 3, it follows that with molar ratios of hydrazine and dicarboxylic acid of 1 : 1 and 1 : 2, salts of constant composition are obtained with a component ratio of 1 : 1. With excess hydrazine (a ratio of 2 : 1), the composition of the salts with a component ratio of 1 : 1 is maintained for salts of sebacic and azelaic acids. For salts of adipic and succinic acids, in this case the component ratio is 2 moles of hydrazine to 1 mole of acid. They were isolated from an alcohol solution as an oil, which slowly crystallized after heating in vacuum to form crystals that deliquesced in air.

Thus, in contrast to diamines, hydrazine forms salts of constant composition with only some dicarboxylic acids. There are dicarboxylic acids with which hydrazine forms salts of two types: $N_2H_4H_2B$ and $(N_2H_4)_2H_2B$.

It was indicated above that hydrazine can form diacidic salts with mineral acids. It was interesting to determine whether organic salts of hydrazine of the type $N_2H_4H_2B$ also had the properties of the diacidic mineral salts. With this aim, the behavior of the salts in aqueous solution was examined. It was established that crystals of the organic acid were deposited from concentrated aqueous solutions and in potentiometric titration of dilute aqueous solutions of it, 1 mole of the organic acid was titrated with alkali with satisfactory accuracy, as shown by the titration curve of a solution of salt obtained from hydrazine and adipic acid (see the figure). For comparison, the titration curves of 66 salt (hexamethylenediamine + adipic acid) and adipic acid are given.

Consequently, in aqueous solutions the given salts behave as compounds with the formula

TABLE 2

Composition and Structure of Salts Formed by Diamines and Dicarboxylic Acids*

Salt components	Molar ratio diamine and acid	Yield (в %)	Melting point	Found (%)			Empirical formula	Calculated (%)			Formula
				C	H	N		C	H	N	
Hexamethylenediamine Sebacic acid	1 : 1	94	172—173°	60.25	10.22	8.42	$C_{16}H_{34}O_4N_2$	60.37	10.69	8.80	$^+H_3N(CH_2)_6NH_3^+$ $^-OOC(CH_2)_8COO^-$
Hexamethylenediamine Sebacic acid	2 : 1	92	173	59.95	10.32	8.48	$C_{16}H_{34}O_4N_2$	60.37	10.69	8.80	
Hexamethylenediamine Sebacic acid	1 : 1.5	60	172	60.33	10.44	8.52	$C_{16}H_{34}O_4N_2$	60.37	10.69	8.80	
Hexamethylenediamine Adipic acid	1 : 2	90	191—192	54.62	9.81	10.42	$C_{12}H_{26}O_4N_2$	54.96	9.92	10.68	$^+H_3N(CH_2)_6NH_3^+$ $^-OOC(CH_2)_4COO^-$
Hexamethylenediamine Azelaic acid	1 : 1	65	146	59.32	10.43	9.12	$C_{15}H_{32}O_4N_2$	59.21	10.52	9.21	$^+H_3N(CH_2)_6NH_3^+$ $^-OOC(CH_2)_7COO^-$
Hexamethylenediamine Azelaic acid	2 : 1	68	146—147	59.11	10.63	9.58	$C_{15}H_{32}O_4N_2$	59.21	10.52	9.21	
Hexamethylenediamine Azelaic acid	1 : 2	84	146—147	59.26	10.25	9.18	$C_{15}H_{32}O_4N_2$	59.21	10.52	9.21	
Ethylenediamine Sebacic acid	1 : 1	91	162—163	55.28	10.12	10.52	$C_{12}H_{26}O_4N_2$	54.97	9.92	10.68	$^+H_3N(CH_2)_2NH_3^+$ $^-OOC(CH_2)_8COO^-$
Ethylenediamine Sebacic acid	2 : 1	91	161—162	55.36	10.19	10.80	$C_{12}H_{26}O_4N_2$	54.97	9.92	10.68	
Ethylenediamine Sebacic acid	1 : 2	90	161—162	55.46	10.07	10.55	$C_{12}H_{26}O_4N_2$	54.97	9.92	10.68	
Ethylenediamine Azelaic acid	1 : 1	97	145	53.47	9.82	10.89	$C_{11}H_{24}O_4N_2$	53.22	9.67	11.29	$^+H_3N(CH_2)_2NH_3^+$ $^-OOC(CH_2)_7COO^-$
Ethylenediamine Azelaic acid	2 : 1	97	145	53.60	9.98	11.17	$C_{11}H_{24}O_4N_2$	53.22	9.67	11.29	
Ethylenediamine Azelaic acid	1 : 2	80	145—147	53.60	9.98	10.79	$C_{11}H_{24}O_4N_2$	53.22	9.67	11.29	

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*Data obtained with the help of B.I. Khubavii.

TABLE 3

Composition and Structure of Salts Formed by Hydrazine and Dicarboxylic Acids*

Salt components	Molar ratio of hydrazine and acid	Yield (%)	Melting point	N_2H_4 found (in %)	Empirical formula	N_2H_4 calc. (%)	Formula
Hydrazine Sebacic acid	1 : 1	92	103—104°	13.25	$C_{20}H_{44}O_8N_4$	13.67	$N_2H_5^{+}\,{}^{-}OOC(CH_2)_8COO^{-}\,{}^{+}H_5N_2 \cdot HOOC(CH_2)_8COOH$
Hydrazine Sebacic acid	1 : 2	85	103—104	13.46	$C_{20}H_{44}O_8N_4$	13.67	
Hydrazine Sebacic acid	2 : 1	80	102—103	13.35	$C_{20}H_{44}O_8N_4$	13.67	
Hydrazine Azelaic acid	1 : 1	88	88	14.44	$C_{18}H_{40}O_8N_4$	14.54	$N_2H_5^{+}\,{}^{-}OOC(CH_2)_7COO^{-}\,{}^{+}H_5N_2 \cdot HOOC(CH_2)_7COOH$
Hydrazine Azelaic acid	1 : 2	85	87—89	14.38	$C_{18}H_{40}O_8N_4$	14.54	
Hydrazine Azelaic acid	2 : 1	55	88—89	14.62	$C_{18}H_{40}O_8N_4$	14.54	
Hydrazine Adipic acid	1 : 1	85	114	17.85	$C_{16}H_{28}O_8N_4$	17.98	$N_2H_5^{+}\,{}^{-}OOC(CH_2)_4COO^{-}\,{}^{+}H_5N_2 \cdot HOOC(CH_2)_4COOH$
Hydrazine Adipic acid	1 : 2	83	113—115	17.65	$C_{16}H_{28}O_8N_4$	17.98	
Hydrazine Adipic acid	2 : 1	72	Oil and hygroscopic crystals	30.95	$C_8H_{18}O_4N_4$	30.47	$N_2H_5^{+}\,{}^{-}OOC(CH_2)_4COO^{-} \cdot {}^{+}H_5N_2$
Hydrazine Succinic acid	1 : 1	62	120	20.92	$C_8H_{20}O_8N_4$	21.33	$N_2H_5^{+}\,{}^{-}OOC(CH_2)_2COO^{-}\,{}^{+}H_5N_2 \cdot HOOC(CH_2)_2COOH$
Hydrazine Succinic acid	1 : 2	54	120—121	20.83	$C_8H_{20}O_8N_4$	21.33	
Hydrazine Succinic acid	2 : 1	52	Oil and hygroscopic crystals	34.82	$C_4H_{12}O_4N_4$	35.16	$N_2H_5^{+}\,{}^{-}OOC(CH_2)_2COO^{-}\,{}^{+}H_5N_2$

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*Data obtained with the help of T.G. Antonova and Chang Shih-yü.

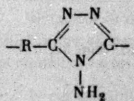
$$N_2H_5{}^{+-}OOCRCOO^{-+}H_5N_2HOOCRCOOH,$$

i.e., as acid salts and in this respect they were similar to salts of hydrazine with mineral acids.

These data indicate that in the salts in which the acidic component is a dicarboxylic acid, the hydrazine is a monoacidic base at all component ratios, including the ratio 1 : 1.

The acid salts readily crystallized from alcohol solutions in contrast to the neutral ones, which separated as an oil that slowly formed hygroscopic crystals.

From the material presented it follows that hydrazine and diamines behave differently in the formation of salts with dicarboxylic acids. The same difference is also noted in the formation of polyamide resins from these compounds. While from different ratios of the dicarboxylic acids and diamines, one can expect only changes in the length of the polymer macromolecules and not changes in the composition, which is characterized by the regular alternation of one acid residue and one diamine residue $-HN-R-NH-CO-R_1-$ $-CO-$; in the case of the polycondensation of hydrazine with dicarboxylic acids we observe the formation of a polymer with a structural group consisting of one acid residue and two hydrazine residues (A) [15].



(A)

Thus, hydrazine behaves as a monacidic base in the formation of polyamide resins, also. This leads to the conclusion that not only the compositions of the salts from which the polyamides are formed, but also the compositions of the polyamide polymers are regulated by the ratio of the dissociation constants of the functional groups of the components.

EXPERIMENTAL

Salts were prepared from sebacic and azelaic acids and diamines by the method described in [1].

98% hydrazine was used for the preparation of salts from dicarboxylic acids and hydrazine. Since salts based on hydrazine crystallized slowly and in poor yields from aqueous alcohol solutions, they were obtained from 96% alcohol.

When salts were prepared from hydrazine and adipic and succinic acids in a molar ratio of 2 : 1, an oil precipitated. The oil was separated from the alcohol and heated in vacuum (5-10 mm) on a boiling water bath for one hour to remove traces of alcohol and water. The oil crystallized on standing.

The amount of hydrazine in the salts was determined directly by the iodate method, using a solvent [16].

SUMMARY

1. It was established that the composition of salts of diamines and azelaic and sebacic acids, prepared with various molar ratios of the starting reagents, was constant and this agrees with previous conclusions [1] on salts of a series of other dicarboxylic acids.

2. With sebacic and azelaic acids, hydrazine forms salts which contain equimolecular amounts of the base and the acid. Adipic and succinic acids form such salts only in the absence of excess hydrazine. In the latter case, the presence of excess hydrazine causes the formation of salts with the composition of 2 moles of hydrazine to 1 mole of acid.

3. It was established that hydrazine behaves as a monoacidic base in aqueous solutions of salts composed of hydrazine and a dicarboxylic acid in equimolecular amounts.

4. The composition of polyamide resins, formed from dicarboxylic acids and diamines or hydrazine, apparently, similarly to the composition of the salts of the corresponding compounds, is controlled by the values of the dissociation constants of the starting materials.

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INVESTIGATION OF HETEROCYCLIC N-OXIDES

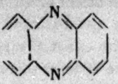
VI. POLAROGRAPHIC REDUCTION OF SOME N-OXIDES OF PHENAZINES AND ACRIDINES

O.N. Nechaeva and Z.V. Pushkareva

N-Oxides of nitrogen-containing heterocyclic compounds are interesting in many connections and, in particular, some of them are of interest as physiologically active substances [1-3]. The N-oxides of the pyridine and quinoline series have been studied in most detail [4].

In our previous reports we described the results of the synthesis and systematic study of N-oxides of more complex heterocyclic systems (acridine, quinoxaline, phenazine and others) [5-8]. One of us and L.V. Variukhina [7] were able to use the polarographic method to establish the relation between the structure of the molecule and the ease of reduction of the N → O bond.

In developing these investigations, we examined the polarographic reduction of compounds (IV)-(XI) of the phenazine series and (XIV)-(XXV) of the acridine series, some of which were synthesized for testing their action on the organism causing Brucella infection [9].



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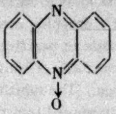

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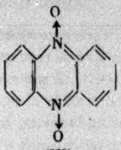

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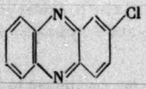

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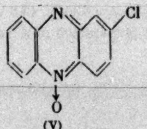

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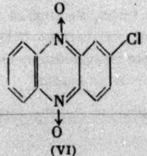

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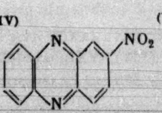

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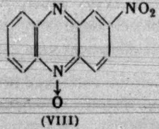

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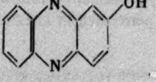

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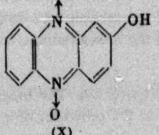

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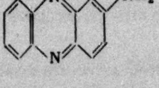

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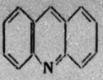

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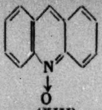

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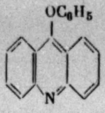

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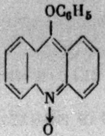

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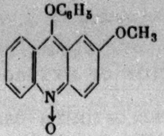

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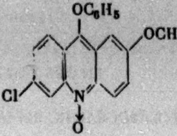

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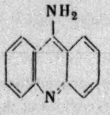

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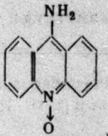

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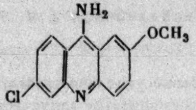

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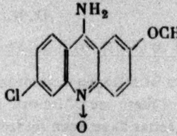

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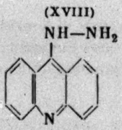

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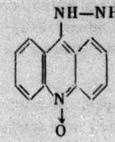

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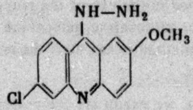

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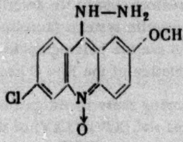


(XXV)

The phenazine derivatives were synthesized so as to follow the effect of different substituents on the stability of the N → O bond relative to reduction at a dropping mercury electrode and on the capacity for reduction of the heterocyclic system itself. A study was made in parallel of the effect of substituents on the biological activity of the N-oxide (II) and dioxide of phenazine (III), of which the latter is more active than "acrichin" (atebrin) as regards the organism causing Brucella infection. The substituents chosen were Cl, NH_2, OH and the electron acceptor group NO_2. All the substituents were introduced into the β-position of the phenazine ring.

In the acridine series, we studied some compounds which we were the first to prepare [9] – N-oxides of 9-amino and 9-hydrazino derivatives, (XIX), (XXI), (XXIII), (XXV), and also N-oxides of 9-phenoxy derivatives (XV)-(XVII), which are intermediates in the preparation of 9-amino and 9-hydrazino derivatives and are of interest in themselves to some extent.

Both in the phenazine and the acridine series, we also studied the unoxidized base, corresponding to each of the N-oxides.

Substances (IV)-(XI), and also (XIV), (XVII), (XVIII), (XX), (XXII) were synthesized by methods described in the literature; the syntheses of substances (XV), (XVI), (XIX), (XXI), and (XXIII)-(XXV) were described in a previous communication [9]. All substances were carefully purified by recrystallization to constant melting point.

The polarographic reduction was performed in a Heyrovsky micropolarograph with which the curves of current strength against voltage were obtained automatically and recorded photographically. The measurements for the acridine derivatives were performed with a galvanometer sensitivity of 1/30 and 1/50 and for the phenazine derivatives, a sensitivity of 1/100. The bulk of the compounds were polarographed at a concentration of $1 \cdot 10^{-3}$ M. The exceptions were 2-hydroxyphenazine and the dioxide of 2-hydroxyphenazine, which were reduced at $1 \cdot 10^{-4}$ M concentration due to their low solubility. All the measurements were performed in alcohol solution in an acetate buffer.

The polarographic curves are shown in Figs. 1-20. The measurement results are given in Table 1. All the half-wave potential values ($E_{1/2}$) are relative to the potential of a saturated calomel electrode (s.c.e.).

TABLE 1

Formula No. in text	Name of substance	Melting point	Concentration (M)	Half-wave potential (relative to a saturated calomel electrode) (V)	Limiting diffusion current (mA)
(I)	Phenazine	171°	$1 \cdot 10^{-3}$	−0.364	5.00
(II)	Phenazine N-oxide	224	$1 \cdot 10^{-3}$	−0.218, −0.382	3.50, 3.10
(III)	Phenazine dioxide	190—191	$1 \cdot 10^{-3}$	−0.218, −0.364	7.77, 4.04
(IV)	2-Chlorophenazine	139	$1 \cdot 10^{-3}$	−0.42	5.70
(V)	2-Chlorophenazine N-oxide	174—175	$1 \cdot 10^{-3}$	−0.22, −0.42	5.75, 5.72
(VI)	2-Chlorophenazine dioxide	190—191	$1 \cdot 10^{-3}$	−0.27, −0.47	12.50, 6.25
(VII)	2-Nitrophenazine	217	$1 \cdot 10^{-3}$	−0.25, −0.69	3.64, 15.10
(VIII)	2-Nitrophenazine N-oxide	203	$1 \cdot 10^{-3}$	−0.24, −0.72	9.90, 15.20
(IX)	2-Hydroxyphenazine	254	$1 \cdot 10^{-4}$	−0.45	0.57
(X)	2- " " dioxide	280	$1 \cdot 10^{-4}$	−0.30, −0.45	3.11, 1.56
(XI)	2-Aminophenazine	287	$1 \cdot 10^{-3}$	−0.54	6.50
(XII)	Acridine	107	$1 \cdot 10^{-3}$	−0.618	2.08
(XIII)	Acridine N-oxide	169 (decomp)	$1 \cdot 10^{-3}$	−0.854	4.66
(XIV)	9-Phenoxyacridine	131	$1 \cdot 10^{-3}$	−0.74, −1.57	3.64, 6.50
(XV)	9-Phenoxyacridine N-oxide	152	$1 \cdot 10^{-3}$	−0.82, −1.60	2.85, 2.90
(XVI)	2-Methoxy-9-phenoxyacridine N-oxide	138	$1 \cdot 10^{-3}$	−0.81, −1.50	5.70, 4.41
(XVII)	2-Methoxy-6-chloro-9-phenoxyacridine N-oxide	175	$1 \cdot 10^{-3}$	−0.80, −1.54	3.12, 1.88
(XVIII)	9-Aminoacridine	236	$1 \cdot 10^{-3}$	−1.21, −1.51	4.80, 0.91
(XIX)	9-Aminoacridine N-oxide	223	$1 \cdot 10^{-3}$	−0.98, −1.24, −1.54	2.89, 3.38, 0.92
(XX)	2-Methoxy-6-chloro-9-aminoacridine	250	$1 \cdot 10^{-3}$	−1.20, −1.50	4.58, 0.91
(XXI)	2-Methoxy-6-chloro-9-aminoacridine N-oxide	237	$1 \cdot 10^{-3}$	−0.98, −1.25, −1.51	3.65, 4.68, 1.30
(XXII)	9-Hydrazinoacridine	169	$1 \cdot 10^{-3}$	−0.96, −1.30	2.87, 4.75
(XXIII)	9-Hydrazinoacridine N-oxide	168	$1 \cdot 10^{-3}$	−0.98, −1.24	2.87, 3.90
(XXIV)	2-Methoxy-6-chloro-9-hydrazinoacridine	161	$1 \cdot 10^{-3}$	−0.70, −1.27	1.17, 3.98
(XXV)	2-Methoxy-6-chloro-9-hydrazinoacridine N-oxide	171	$1 \cdot 10^{-3}$	−0.66, −1.44	2.85, 3.90

Phenazine Derivatives

As is known, phenazine is a heterocycle which readily undergoes oxidation-reduction conversions. It is readily reduced at a mercury dropping electrode at $E_{1/2} = -0.364$ V. According to data in [7], the N → O bond in phenazine N-oxide is reduced at a mercury dropping electrode more readily than in the N-oxides of other heterocycles, giving a half-wave potential, which is strongly displaced toward positive values (−0.22 V).

The reduction of phenazine N-oxides, which do not contain readily reducible groups as substituents, proceeds in two stages, giving a polarographic curve with two waves (Figs. 2, 3 and 7). Here the first wave refers to the reduction of the N → O bond and the second to the reduction of the phenazine system to the dihydrophenazine. With a nitro group present in the molecule, one would expect the appearance of three waves, though the polarographic curve (Fig. 5) has only two waves. This is apparently due to the fact that in this molecule the N → O bond and the phenazine system are reduced at identical half-wave potential values (−0.24 V). In fact, the height of the first wave in the case of the N-oxide is almost twice as great as the first wave for the unoxidized base (Figs. 4 and 5).

The unoxidized bases give polarographic curves with one wave (Figs. 1, 6 and 8). The exception is 2-nitrophenazine and the second wave on its polarogram corresponds to the reduction of the nitro group (Fig. 4).

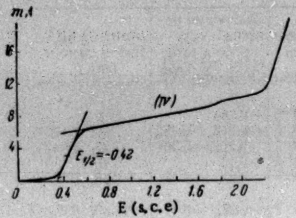


Fig. 1. Polarogram of 2-chlorophenazine.

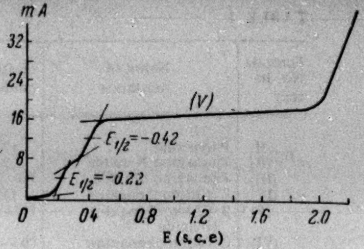


Fig. 2. Polarogram of 2-chlorophenazine N-oxide.

Data presented in Table 1 show that the reduction potential of the N → O bond changes, depending on the character of the substituent in the phenazine N-oxide ring. The introduction of chlorine into position 2 of phenazine N-oxide has hardly any effect on the capacity of the N → O bond for reduction at a mercury dropping electrode. Thus, the half-wave potential of 2-chlorophenazine N-oxide is −0.22 V, for 2-chlorophenazine dioxide it is −0.27 V and −0.22 V for unsubstituted phenazine N-oxides (Figs. 2 and 3). The introduction of a nitro group into the same position gives approximately the same effect. The results are changed when the substituents are the electron donor groups OH and NH_2, which produce a displacement of the half-wave potential toward more negative values.

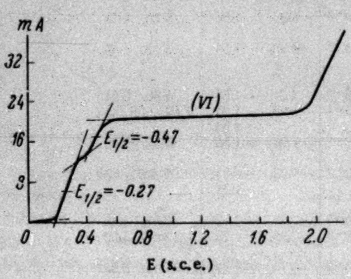


Fig. 3. Polarogram of 2-chlorophenazine dioxide.

A similar picture was also observed on analyzing the half-wave potentials referring to the phenazine molecules themselves (Table 2) (the second wave in the case of the N-oxides and the first wave in the case of the unoxidized bases).

As can be seen, conjugation of an electron-donor group with the ring leads to a considerable increase in the electron density at the hetero atom, making its reduction at a mercury dropping electrode more difficult. On the other hand, the electron-acceptor nitro group facilitates the reduction.

In the synthesis of N-oxides for biological testing, there is interest in the general result: by introducing substituents into the phenazine ring it is possible to affect the stability of the N → O bond with respect to reduction (it is known that some N-oxides, which have biological activity in vitro, are easily inactivated in vivo due to the loss of the oxide oxygen .

TABLE 2

Substance*	Phenazine	2-Chloro-phenazine	2-Nitro-phenazine	2-Hydroxy-phenazine	2-Amino phenazine
$E_{1/2}$ (V)	−0.36	−0.37	−0.20	−0.45	−0.54

Acridine Derivatives

By comparing polarograms for 9-chloroacridine N-oxide and unoxidized 9-chloroacridine derivatives, it was shown [7] that in contrast to acridine N-oxide (XIII), they gave two polarographic waves and the second of these was due to the chemical features of the heterocycle itself.

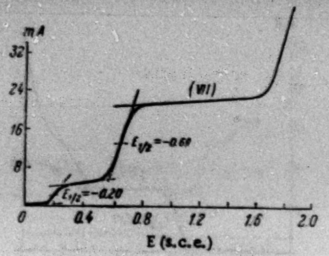


Fig. 4. Polarogram of 2-nitrophenazine.

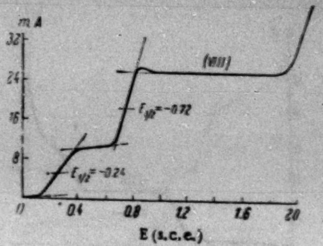


Fig. 5. Polarogram of 2-nitrophenazine N-oxide.

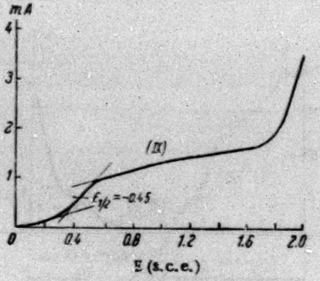


Fig. 6. Polarogram of 2-hydroxyphenazine.

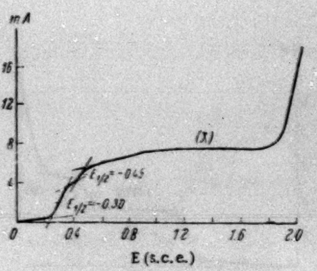


Fig. 7. Polarogram of 2-hydroxyphenazine dioxide.

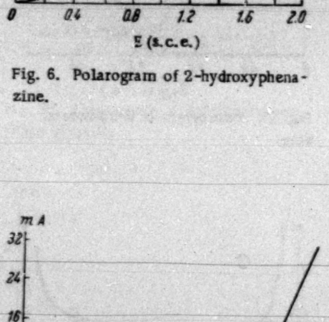


Fig. 8. Polarogram of 2-aminophenazine.

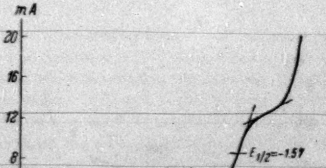


Fig. 9. Polarogram of 9-phenoxyacridine.

By considering the data on polarographic reduction, presented in Table 1, one can make the following observations.

1. Like 9-chloroacridine and in contrast to unsubstituted acridine, 9-phenoxyacridine (XIV) gives two polarographic waves. The value of $E_{1/2}$ for the first wave is close to the half-wave potential of acridine (−0.75 and −0.62 V, respectively), while the second stage of the reduction proceeds at strongly negative half-wave potentials (−1.58 V), giving a definite wave on the polarogram (Fig. 9).

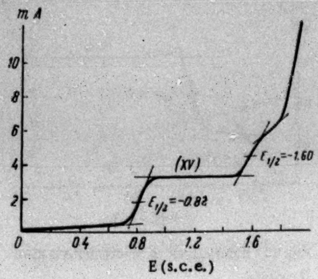


Fig. 10. Polarogram of 9-phenoxyacridine N-oxide.

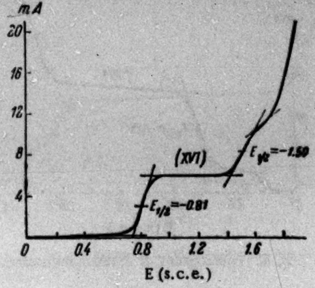


Fig. 11. Polarogram of 2-methoxy-9-phenoxyacridine N-oxide.

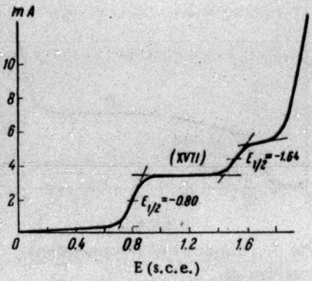


Fig. 12. Polarogram of 2-methoxy-6-chloro-9-phenoxyacridine N-oxide.

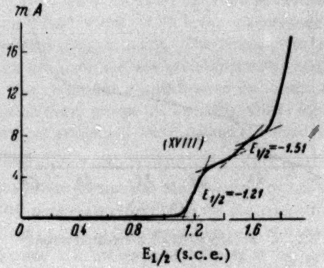


Fig. 13. Polarogram of 9-aminoacridine.

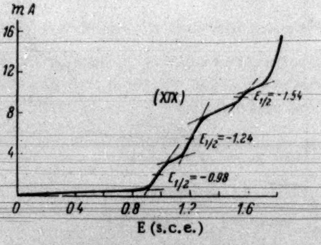


Fig. 14. Polarogram of 9-aminoacridine N-oxide.

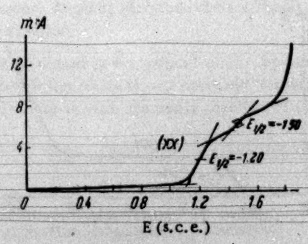


Fig. 15. Polarogram of 2-methoxy-6-chloro-9-aminoacridine.

Unexpectedly, 9-phenoxyacridine N-oxides also give two, and not three, waves, when the $E_{1/2}$ value of the second wave remains almost unchanged (of the order of −1.5 to −1.6 V) and the first stage of the reduction proceeds at a potential of from −0.80 to −0.82 V, i.e., with approximately the same ease as the reduction of the N → O bond in unsubstituted acridine N-oxide (−0.85 V) (Figs. 10-12). It is still unclear why the wave characterizing the reduction of the acridine ring is absent from the polarogram.

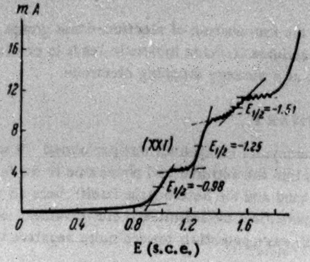


Fig. 16. Polarogram of 2-methoxy-6-chloro-9-aminoacridine N-oxide.

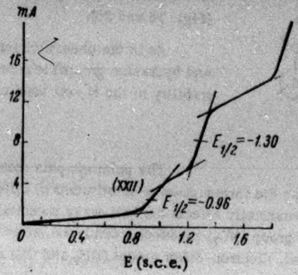


Fig. 17. Polarogram of 9-hydrazinoacridine.

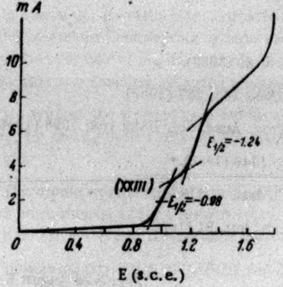


Fig. 18. Polarogram of 9-hydrazinoacridine N-oxide.

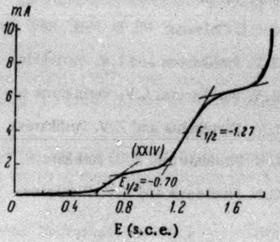


Fig. 19. Polarogram of 2-methoxy-6-chloro-9-hydrazinoacridine.

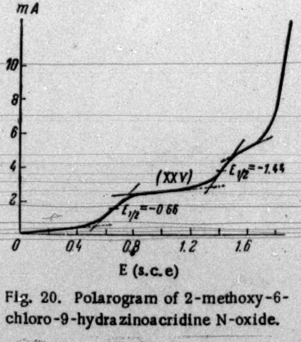


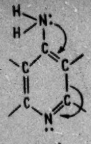
Fig. 20. Polarogram of 2-methoxy-6-chloro-9-hydrazinoacridine N-oxide.

2. 2-Aminoacridine (XVIII) and 2-methoxy-6-chloro-9-aminoacridine (XX) are reduced at half-wave potentials, which are strongly displaced toward more negative values (−1.21 and −1.20 V instead of −0.618 V for acridine), apparently as a result of conjugation in the system (XXVI) and a considerable increase in the electron density at the hetero atom. In addition, the polarograms show a second indistinct wave with $E_{1/2}$ = −1.51 and −1.50 V (Figs. 13 and 15).

The 9-aminoacridine N-oxides (XIX) and (XXI) are reduced in two stages (there is also an indistinct third wave at strongly negative potentials). The first stage corresponds to the reduction of the N → O bond (−0.98 V) and the second to the reduction of the acridine ring (−1.24 and −1.25 V) (Figs. 14 and 16).

3. The reduction of 9-hydrazinoacridines (XXII) and (XXIV) goes in two stages and the polarograms show two quite distinct waves (Figs. 17 and 19).

In all probability, the first half-wave potential refers to the reduction of the hydrazine link (considering data on the polarographic reduction of arylhydrazines). On going from the unoxidized bases to the N-oxides, as



(XXVI)

in the case of the 9-phenoxy derivatives, the polarograms show only two reduction stages (Figs. 18 and 20).

As in the phenazine series, in general the introduction of electron-donor groups (amino and hydrazino groups) into position 9 of the acridine N-oxide molecule leads to considerable stability of the N → O bond toward reduction at a mercury dropping electrode.

SUMMARY

The polarographic reduction of 20 heterocyclic compounds was performed. It was shown that the introduction of substituents of different characters into the acridine and phenazine N-oxide molecules substantially affects the half-wave potential of the N → O bond and the heterocycle itself; here an electron-acceptor group (NO_2) produces a displacement of the half-wave potentials toward more positive values; on the other hand, electron-donor groups (NH_2 and OH) displace the half-wave potentials toward more negative values.

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INVESTIGATION OF HETEROCYCLIC N-OXIDES

VII. DIPOLE MOMENTS AND CHEMICAL FEATURES OF SOME DERIVATIVES OF PHENAZINE AND ACRIDINE N-OXIDES

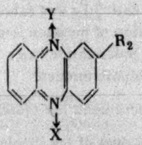
Z.V. Pushkareva and O.N. Nechaeva

In one of our previous communications, we described the results of measuring the dipole moments of the N-oxides of various heterocyclic systems and demonstrated the dependence of the dipole moment of the N → O bond on the structure of the heterocycle and the interrelation of the polarity of the N → O bond and its capacity for reduction at a mercury dropping electrode [1].

We synthesized a series of N-oxides of phenazine (I) and acridine (VIII), containing various substituents in the ring, for testing their action on the organism causing Brucella infection [2] and to reduce them polarographically [3].

The dipole moments of a considerable number of these N-oxides and the unoxidized bases corresponding to them were studied and the present article is devoted to the results of these measurements [for the phenazine derivatives (II)-(VII) and the acridine derivatives (IX)-(XVI)].

Substances (II)-(VII), (IX), (XII) and (XIII) were synthesized by methods described in the literature. We prepared and described [2] substances (X), (XI), (XIV)-(XVI) previously. All the substances were carefully purified to constant melting point.



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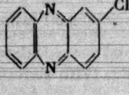

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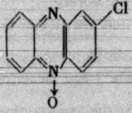

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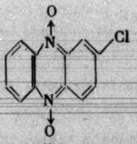

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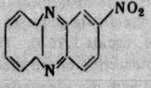

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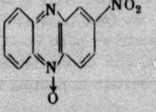

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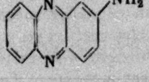

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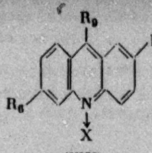
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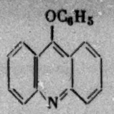
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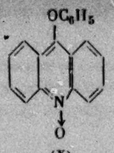
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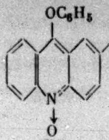
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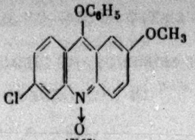
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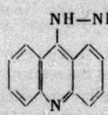
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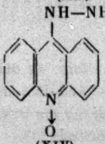
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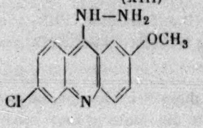
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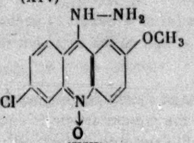

(XVI)

The dielectric constants ε were determined by the heterodyne method in benzene solutions at 25° in an apparatus where the density d was measured simultaneously with a torsion balance.

The total polarization at infinite dilution (P_∞) was calculated by Hedestrand's method [4] from the experimental data for ε and d. The electron polarization P_e was calculated as the molecular refraction; the refraction of N → O was calculated from the refraction of pyridine N-oxide. The atomic polarization P_a was neglected, as, for the compounds studied, the orientation polarization had a large value and the values of P_a included in it had no substantial effect on the value of the dipole moment.

The results of the dipole-moment measurements are presented in Table 1.

For comparison with the experimental values of the dipole moments, the vector sums of the bond moments were calculated ($\mu_{calc.}$), starting from the dipole moments of the simplest molecules and bonds. In the cases where different molecular configurations were theoretically possible, vector sums were calculated for all these configurations (only the calculated values which are closest to the experimental values are given in Tables 2 and 3).

For convenience in discussion, all the results for the experimental and calculated values of dipole moments for phenazine (I) derivatives are given in Table 2 and those for acridine (VIII) derivatives, in Table 3.

The data presented in Table 2 show that the introduction of various substituents into position 2 of the phenazine molecule leads to a large dipole moment (Cl – 2.46 D, NO_2 – 6.61 D, NH_2 – 6.72 D), while the dipole moment of unsubstituted phenazine equals zero (No. 1, Table 2) and the dipole moment of phenazine N-oxide (No. 2, Table 2), which contains the comparatively polar N → O bond, equals 1.76 D. This is apparently connected with the asymmetry of the molecule, with the considerable interaction of the electron system of the substituent with the electron system of the heteroatom in position 10, and with the elongation of the dipole arising as a result of this.

The dipole moment of 2-chlorophenazine N-oxide (No. 4, Table 2) is only slightly greater than the dipole moment of the unoxidized base (2.69 D instead of 2.46 D) and its value is close to the vector sum of the moments

TABLE 1

Formula No. in text	Name of substance	P_∞	P_e	$\mu_{exp} \cdot 10^{18}$
(II)	2-Chlorophenazine	179.966	55.318	2.46
(III)	2-Chlorophenazine N-oxide	209.654	60.288	2.69
(IV)	2-Chlorophenazine dioxide	271.672	65.258	3.16
(V)	2-Nitrophenazine	956.877	52.938	6.61
(VI)	2-Nitrophenazine N-oxide	764.089	57.908	5.85
(VII)	2-Aminophenazine	986.539	53.878	6.72
(IX)	9-Phenoxyacridine	217.408	97.947	2.40
(X)	9-Phenoxyacridine N-oxide	553.502	102.917	4.67
(XI)	2-Methoxy-9-phenoxyacridine N-oxide	696.147	108.232	5.33
(XII)	2-Methoxy-6-chloro-9-phenoxyacridine N-oxide	1011.887	112.970	6.60
(XIII)	9-Hydrazinoacridine	820.753	79.135	5.99
(XIV)	9-Hydrazinoacridine N-oxide	909.346	84.105	6.32
(XV)	2-Methoxy-6-chloro-9-hydrazinoacridine	1238.047	89.315	7.45
(XVI)	2-Methoxy-6-chloro-9-hydrazinoacridine N-oxide	1493.718	94.285	8.23

TABLE 2

Expt. No.	Formula No. in text	X	Y	R_1	$\mu_{exp} \cdot 10^{18}$	$\mu_{calc} \cdot 10^{18}$
1	—	—	—	—	0	0
2	—	→ O	—	—	1.76 [1]	—
3	(II)	—	—	Cl	2.46	1.55
4	(III)	→ O	—	Cl	2.69	2.75
5	(IV)	→ O	→ O	Cl	3.16	2.86
6	(V)	—	—	NO_2	6.61	3.95
7	(VI)	→ O	—	NO_2	5.85	4.89
8	(VII)	—	—	NH_2	6.72	1.53

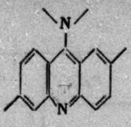
of the C – Cl and N → O bonds (2.75 D). On the other hand, the dipole moment of 2-nitrophenazine N-oxide is less than the dipole moment of the unoxidized base by approximately 0.8 D. 2-Aminophenazine has the greatest polarity ($\mu_{exp.}$ = 6.72 D).

The data given in Table 3 show that the molecules of the 9-phenoxy derivative are more polar than the corresponding 9-chloro derivative. The introduction of a methoxyl group into position 2 and a chlorine into position 6, considerably increases the dipole moment of 9-phenoxyacridine derivative. The vector sums of the moments, calculated for free rotation of the phenoxy groups, are the closest to the experimental values.

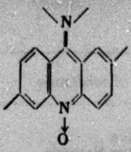
9-Hydrazinoacridine has a very large dipole moment (5.99 D), which considerably exceeds the dipole moment of 9-aminoacridine (4.13 D). The calculated dipole moment is much less than the experimental (the difference is 2.57 D). The introduction of a methoxyl group into position 2 and a chlorine into position 6 of the acridine molecule, as in the case of 9-phenoxy derivatives, sharply increases the dipole moment of the molecule.

In all cases, there was an increase in the dipole moments in going from the unoxidized derivatives of acridine to their N-oxides.

Comparison of our data, characterizing the polarity of molecules of 9-hydrazinoacridines, with data on the dipole moments of 9-aminoacridines [5], leads to the conclusion that molecules of type (A) are unusually polar and that



(A)



(B)

the introduction of an oxide oxygen into them further increases the dipole moment of the molecule [type (B)].

Taking into account the fact that among acridine derivatives of type (A) there are many physiologically active substances, one may consider that substances of type (B), the first representative of which we synthesized recently, may acquire even greater interest for testing their biological activities, as the introduction of an oxide oxygen generally imparts valuable biological properties.

TABLE 3

Expt. No.	Formula No. in text	X	R_9	R_2	R_6	$\mu_{exp.} \cdot 10^{18}$	$\mu_{calc.} \cdot 10^{18}$
1	—	—	—	—	—	1.84 [1]	—
2	—	→ O	—	—	—	4.08 [1]	—
3	—	—	Cl	—	—	0 [1]	—
4	(IX)	—	OC_6H_5	—	—	2.40	2.56
5	(X)	→ O	OC_6H_5	—	—	4.67	4.34
6	(XI)	→ O	OC_6H_5	OCH_3	—	5.33	4.97
7	(XII)	→ O	OC_6H_5	OCH_3	Cl	6.60	6.55
8	(XIII)	—	$NH-NH_2$	—	—	5.99	3.42
9	(XIV)	→ O	$NH-NH_2$	—	—	6.32	5.35
10	(XV)	—	$NH-NH_2$	OCH_3	Cl	7.45	5.08
11	(XVI)	→ O	$NH-NH_2$	OCH_3	Cl	8.23	5.21
12	—	—	NH_2	—	—	4.13 [5]	3.28
13	—	—	NH_2	OCH_3	Cl	6.73 [5]	4.95

SUMMARY

1. Measurements were made of the dipole moments of 14 substances which are derivatives of phenazine and acridine and their N-oxides.

2. An investigation was made of the interaction of the N → O bond in phenazine and acridine N-oxides with various substituents in the heterocyclic ring.

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INVESTIGATION OF STRUCTURAL FEATURES AND CHEMICAL CONVERSIONS OF CARBAZOLE AND SOME OF ITS DERIVATIVES

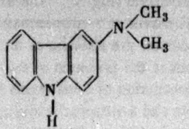
II. SOME PROPERTIES OF 3-AMINOCARBAZOLE AND ITS DERIVATIVES

S.I. Omel'chenko and Z.V. Pushkareva

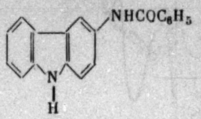
Despite the fact that many papers have been devoted to the synthesis of 3-aminocarbazole, the properties of this compound have not been studied in detail. There are only descriptions of the acetylation reaction [1, 2] and of some 9-substituted 3-aminocarbazoles with physiological activity [3-6].

In order to extend the knowledge of 3-aminocarbazole, we studied the alkylation, acylation and carboxymethylation of this compound and also the ultraviolet absorption spectra of all the derivatives obtained.

The methylation with dimethyl sulfate proceeded at room temperature in an alkaline medium with the formation of 3-dimethylaminocarbazole (I) with m.p. 135-140° (decomp.).



(I)

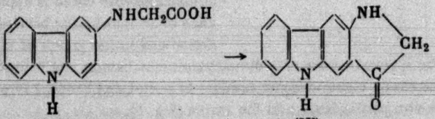


(II)

Depending on the conditions, the acetylation of 3-aminocarbazole with acetic anhydride could give either the mono-, di- or triacetyl derivatives.

The monobenzoyl derivative (II) could be obtained by reacting 3-aminocarbazole with benzoyl chloride in the presence of sodium alcoholate.

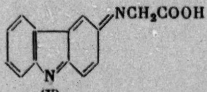
We were interested in carboxymethylation for the possibility of obtaining 3-carbazylglycine (III), an analog of phenylglycine, which is a starting material in the synthesis of indigoid dyes.



(III) (IV)

It was found that 3-aminocarbazole did not react with chloroacetic acid, despite the fact that all possible conditions were tried. Compound (III) was obtained only when bromoacetic acid was used as the alkylating agent; the product was isolated as a greenish-gray powder with m.p. 220° (decomp.).

Attempts to close the oxindole ring [(III) → (IV)] both by alkaline fusion and with the addition of various water-abstracting agents in an acid medium were unsuccessful. Carbazylglycine showed extreme stability in alkaline media and was decomposed quite quickly in acids. In working with this compound we noticed its interesting tendency to change into a black product with a sharp m.p. of 150° on standing in air in organic solvents; in all probability this product was the corresponding quinonediimine (V).



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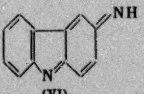

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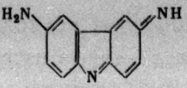

(VII)

Subsequently, black products were obtained from unsubstituted 3-aminocarbazole (VI) and 3,6-diaminocarbazole (VII) under slightly different conditions.

Comparison of the ultraviolet absorption spectra of the black products obtained with the spectra of carbazole and 3-aminocarbazole (Fig. 1) confirmed the hypothesis that these substances had structures of the quinonediimine type (their spectra were similar to each other and differed sharply from the spectra of the original carbazole and 3-aminocarbazole).

Considering the singularity of 3-aminocarbazole, observed in studying its simple reactions, attempts were made to explain the peculiarities of its structure by examining its ultraviolet absorption spectra.

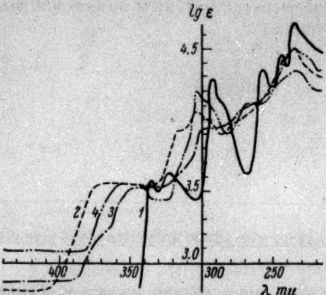

Fig. 1. Absorption spectrum curves: 1) carbazole; 2) quinonediimine of 3-aminocarbazole; 3) quinonediimine of 3-carbazylglycine; 4) quinonediimine of 3,6-diaminocarbazole.

As the idea of nitro derivatives of carbazole having a quinoid structure in an alkaline medium is put forward in the literature [7], we studied the spectra of 3-nitrocarbazole derivatives (Fig. 2). The unexpected similarity of the spectral curves of 3-nitrocarbazole in alkaline and neutral media indicates the absence of the quinoid form in alkaline solutions, or the presence of the latter in a neutral medium. The introduction of substituents into position 9 (9-methylcarbazole and 9-nitrocarbazole), which excludes the possibility of quinoid-form formation, did not produce any essential changes in the spectral curves (Fig. 2), indicating the absence of quinoid forms of 3-nitrocarbazole.

The spectrum of 3-aminocarbazole (Fig. 3) is characterized by the presence of a deep minimum at 312 mμ; the sections to the right and to the left of the main maximum in the carbazole spectrum are considerably changed. 3-Aminocarbazole hydrochloride has a spectrum which is similar to the carbazole spectrum (Fig. 3). The peculiarity of the 3-aminocarbazole curve is apparently connected with the presence of an interaction between the electron systems of the amino and imino groups of the compound and this is confirmed by examining the spectral curves of 3-dimethylaminocarbazole and 9-methyl-3-aminocarbazole (Fig. 4). The introduction of such strong electron-donor residues as acetyl and benzoyl into the amino group, leads to a substantial change in the original spectrum of the amine (Fig. 5).

EXPERIMENTAL

3-Dimethylaminocarbazole (I). 0.5 ml of dimethyl sulfate and 1 ml of 35% NaOH was added to a mixture of 30 ml of water, 20 ml of acetone and 1 g of 3-aminocarbazole; the mixture was shaken for 15 minutes, second portions of dimethyl sulfate and alkali added and shaking continued for one hour. The whole precipitate dissolved. The acetone was distilled off on a water bath, the aqueous solution adjusted to pH 9 and the brown oil which formed was separated from the aqueous layer and dissolved in anhydrous alcohol. (I) was precipitated from the alcohol solution with absolute ether in the form of a white, finely crystalline precipitate with m.p. 135-140°.

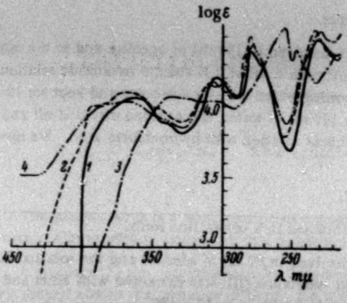

Fig. 2. Absorption spectrum curves: 1) 3-nitrocarbazole; 2) N-methyl-3-nitrocarbazole; 3) N-nitroso-3-nitrocarbazole; 4) 3-nitrocarbazole in an alkaline medium.

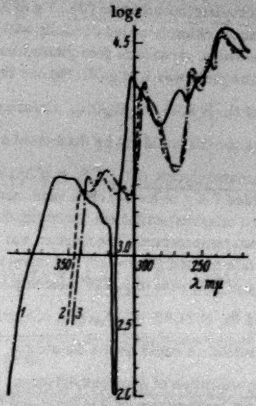

Fig. 3. Absorption spectrum curves: 1) 3-aminocarbazole; 2) 3-aminocarbazole hydrochloride; 3) carbazole.

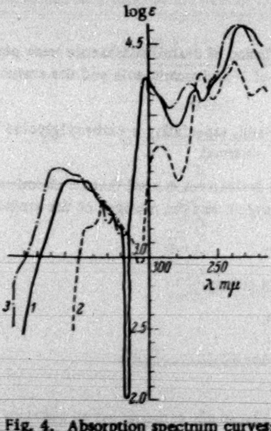

Fig. 4. Absorption spectrum curves: 1) 3-aminocarbazole; 2) 3-dimethylaminocarbazole; 3) N-methyl-3-aminocarbazole.

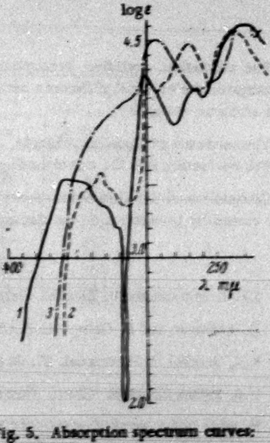

Fig. 5. Absorption spectrum curves: 1) 3-aminocarbazole; 2) 3-monoacetylaminocarbazole; 3) 3-benzoylaminocarbazole.

The yield was 0.6 g (57%). Substance (I) could not be diazotized, indicating the presence of substituents on the amino group.

Found %: N 6.87. $C_{13}H_{11}ON$. Calculated %: N 7.10.

3-Benzoylaminocarbazole (II). 1 g of 3-aminocarbazole was mixed with 15 ml of sodium alcoholate and 6 ml of benzoyl chloride added carefully with stirring and cooling. The mixture was kept without stirring for a day and the white, crystalline precipitate filtered off, washed with water and recrystallized from alcohol and acetone. The yield was 1.20 g (81.7%) and the m.p. 265°.

Found %: N 9.95. $C_{19}H_{14}ON_2$. Calculated %: N 9.82.

Substance (II) could not be diazotized and would not couple.

3-Carbazylglycine (III). 1.82 g of 3-aminocarbazole was dissolved in 100 ml of acetone and to the solution was added 1.4 g of bromoacetic acid, neutralized in the cold with 5 ml of 2 N sodium hydroxide solution. The reaction mixture was shaken for 30 minutes, heated on a boiling water bath for 0.5 hours and kept for 12 hours at room temperature. The solution was then diluted with 100 ml of water, the acetone distilled off and the precipitate formed filtered off and reprecipitated from ammonia solution with hydrochloric acid. We obtained 1.2 g of (III) with m.p. 120° (decomp.).

Found %: N 11.66. $C_{14}H_{12}O_2N_2$. Calculated %: N 11.57.

The substance could not be diazotized. It could not be obtained in a crystalline form.

Quinonediimine of 3-carbazylglycine. 2 g of (III) was dissolved in 50 ml of alcohol and the solution kept in air at room temperature for 3-4 hours and diluted with water; substance (III) was extracted with ether and distillation of the ether extract yielded 1.5 g of a uniform black product with m.p. 175-180°.

Found %: N 11.52. $C_{14}H_{10}O_2N_2$. Calculated %: N 11.76.

The quinonediimines of 3-aminocarbazole and 3,6-diaminocarbazole were prepared similarly, though the alcohol solutions of the starting materials were shaken in air for 1.5 days.

The ultraviolet absorption spectra were measured on an SF-4 spectrophotometer using alcohol solutions.

SUMMARY

1. The alkylation, acylation, benzoylation and carboxymethylation of 3-aminocarbazole were performed and demonstrated the essential difference between the amino group of 3-aminocarbazole and the amino groups of normal aromatic amines.

2. The tendency of 3-aminocarbazole, 3,6-diaminocarbazole and, especially, 3-carbazylglycine to undergo oxidative conversion into the corresponding quinonediimines was observed.

3. Comparison of the ultraviolet spectra of 3-aminocarbazole derivatives showed that its chemical singularity was caused by interaction of the electron systems of the heteroatom and the nitrogen of the amino group.

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CATALYTIC DEHYDROCONDENSATION OF TRIALKYLSILANES WITH ALCOHOLS IN THE PRESENCE OF METAL CHLORIDES

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The present work is a continuation of our investigations on the catalytic dehydrocondensation of trialkyl- and triarylsilanes with hydroxy, oxo and polyhydroxy organic compounds.

Previously [1] the catalysts used for dehydrocondensation of R_3SiH with alcohols were alcoholates of the alkali metals and, in the presence of these, the yields of trialkylalkoxysilanes reached 80-90%.

The present report describes the use of small amounts of various metal chlorides, of which the most active were $ZnCl_2$ and $SnCl_2$, in the dehydrocondensation of R_3SiH with alcohols.

The rate of the reaction of R_3SiH with alcohols depended on the nature and the amount of the metal chloride. Increasing the amount of chloride in the reaction mixture from 0.05 to 1 g led to a noticeable growth in the reaction rate, but a further increase did not affect the process. This was tried on the reaction of methanol with triethylsilane at a ratio of 2:1 (Table 1).

TABLE 1*

Catalyst	Amount of catalyst (in g)	Reaction time (in minutes)	Yield of $(C_2H_5)_3SiOCH_3$ (in %)
$ZnCl_2$	1	90	97.7
$CdCl_2$	1	2610	97.2
Cu_2Cl_2	1	2700	0
$SnCl_2$	1	60	98.0
$ZnCl_2$	0.05	4080	96.8
$ZnCl_2$	0.1	3660	97.0
$ZnCl_2$	0.2	960	96.9
$ZnCl_2$	0.5	360	97.7
$ZnCl_2$	3	90	98.4

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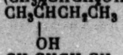
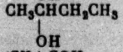
*Experiments at 120-125°.

An increase in the length of the alkyl radical from CH_3 to n-C_4H_9, in alcohols of normal structure, lowered the reaction rate (Table 2, Expts. 1-3 and 5). In the case of radicals with an iso-structure, steric hindrance lowered the reaction rate considerably (Table 2).

In contrast to the dehydrocondensation of R_3SiH with tert.-butyl alcohol in the presence of alkali metals [1], this reaction could not be realized at normal pressure or in an autoclave in the presence of $ZnCl_2$ and $SnCl_2$ (Table 2, Expts. 11 and 12).

The structure of the trialkylsilane also had a substantial effect on the reaction rate (Table 3). When one of the ethyl radicals in triethylsilane was substituted by methyl, the rate of reaction with n-butyl alcohol was increased by a factor of 2 with $SnCl_2$ (Expts. 1 and 3) and a factor of 3.5 with $ZnCl_2$ (Expts. 2 and 4) and with isobutyl alcohol it was increased by a factor of 1.5 in the case of $SnCl_2$ and a factor of 4.5 in the case of $ZnCl_2$.

TABLE 2*

Expt. No.	Formula of alcohol	Formula of trialkylsilane	$MeCl_2$ catalyst (nature of Me)	Reaction time (in min)	Yield of R_3SiOR' (in %)
1	CH_3OH	$(C_2H_5)_3SiH$	Zn	240	98.0
2	CH_3CH_2OH	$(C_2H_5)_3SiH$	Zn	270	96.9
3	$CH_3CH_2CH_2OH$	$(C_2H_5)_3SiH$	Zn	300	98.6
4	$(CH_3)_2CHOH$	$(C_2H_5)_3SiH$	Zn	480	96.1
5	$CH_3CH_2CH_2CH_2OH$	$(C_2H_5)_3SiH$	Zn	330	96.0
6	$(CH_3)_2CHCH_2CH_2OH$	$(C_2H_5)_3SiH$	Sn	60	98.0
7	$(CH_3)_2CHCH_2OH$	$(C_2H_5)_3SiH$	Zn	3600	86.6
8	$(CH_3)_2CHCH_2OH$	$(C_2H_5)_3SiH$	Sn	75	93.4
9	 $CH_3\underset{OH}{\underset{\vert}{C}}HCH_2CH_3$	$CH_3(n.\text{-}C_4H_9)_2SiH$	Zn	540	86.9
10	 $CH_3\underset{OH}{\underset{\vert}{C}}HCH_2CH_3$	$CH_3(n.\text{-}C_4H_9)_2SiH$	Sn	90	91.4
11	$(CH_3)_3COH$	$CH_3(n.\text{-}C_4H_9)_2SiH$	Zn	600	0
12	$(CH_3)_3COH$	$CH_3(n.\text{-}C_4H_9)_2SiH$	Sn	600	0

*Experiments at 120-125°.

TABLE 3

Expt. No.	Formula of trialkylsilane*	$MeCl_2$ catalyst (nature of Me)	Reaction time (in minutes)	Yield of R_3SiOR' (in %)
1	$(C_2H_5)_3SiH$	Sn	60	96.0
2	$(C_2H_5)_3SiH$	Zn	330	96.9
3	$CH_3(C_2H_5)_2SiH$	Sn	30	85.5
4	$CH_3(C_2H_5)_2SiH$	Zn	90	92.9
5	$CH_3(n.\text{-}C_3H_7)_2SiH$	Sn	45	99.3
6	$CH_3(n.\text{-}C_3H_7)_2SiH$	Zn	105	97.3
7	$CH_3(n.\text{-}C_4H_9)_2SiH$	Sn	45	99.3
8	$CH_3(n.\text{-}C_4H_9)_2SiH$	Zn	110	90.3
9	$(C_2H_5)_3SiH$	Sn	75	96.0
10	$(C_2H_5)_3SiH$	Zn	600	96.9
11	$CH_3(C_2H_5)_2SiH$	Sn	45	93.4
12	$CH_3(C_2H_5)_2SiH$	Zn	135	92.7
13	$CH_3(n.\text{-}C_3H_7)_2SiH$	Sn	45	85.7
14	$CH_3(n.\text{-}C_3H_7)_2SiH$	Zn	135	82.0
15	$CH_3(n.\text{-}C_4H_9)_2SiH$	Zn	150	90.0
16	$CH_3(n.\text{-}C_4H_9)_2SiH$	Sn	50	89.9

*Experiments 1-8 were performed with $n\text{-}C_4H_9OH$ and experiments 9-16 with primary isobutyl alcohol. The temperature was 120-125°.

The dehydrocondensation of R_3SiH with alcohols in the presence of alkali metal alcoholates [1] or metal chlorides proceeds by an ion-chain mechanism.

As a result of our experiments we synthesized 13 trialkylalkoxysilanes (seven of them for the first time). The physical properties of the new substances are presented in Table 4. The physical properties of the known silanes corresponded to the properties that we gave for these compounds previously [1].

The method presented of synthesizing trialkylalkoxysilanes by condensing R_3SiH with anhydrous alcohols in the presence of metal chlorides, is a general one for alkoxylation of the Si–H bond. The method makes it possible to obtain trialkylalkoxysilanes in a pure form. As special experiments showed, side products are not formed in this reaction.

TABLE 4

Trialkylalkoxysilanes

Formula	Boiling point	d_4^{20}	n_D^{20}	MR_D*		Molecular weight		Si content (in %)	
				calc.	found	calc.	found	calc.	found
$CH_3(C_2H_5)_2SiOCH_2CH_2CH_2CH_3$ **	172.2°	0.8060	1.4125	54.2	53.9	174.4	175.2, 175.0	16.1	15.8, 16.0
$CH_3(n.\text{-}C_3H_7)_2SiOCH_2CH_2CH_2CH_3$ ***	202.5	0.8094	1.4200	63.4	63.3	202.4	202.2, 202.0	13.9	13.7, 14.0
$CH_3(n.\text{-}C_4H_9)_2SiOCH_2CH_2CH_2CH_3$	235.5	0.8154	1.4272	72.7	72.7	230.5	227.8, 228.0	12.2	12.4, 12.1
$CH_3(C_2H_5)_2SiOCH_2CH(CH_3)_2$	166.5	0.8009	1.4098	54.2	53.9	174.4	173.1, 175.1	16.1	16.0, 15.9
$CH_3(n.\text{-}C_3H_7)_2SiOCH_2CH(CH_3)_2$	197.3	0.8046	1.4172	63.4	63.2	202.4	200.8, 201.8	13.9	14.1, 14.0
$CH_3(n.\text{-}C_4H_9)_2SiOCH_2CH(CH_3)_2$	228.3	0.8114	1.4250	72.7	72.4	230.5	229.0, 227.8	12.2	12.6, 12.3
$CH_3(n.\text{-}C_4H_9)_2SiO\underset{\underset{CH_3}{\vert}}{C}HCH_2CH_3$	226.6	0.8132	1.4260	72.7	72.5	230.5	232.5, 227.4	12.2	12.3, 12.5

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*Molecular refractions were calculated according to data in [4].

**Found %: C 61.8, 61.8; H 12.9, 12.8. $C_9H_{22}SiO$. Calculated %: C 62.0; H 12.8.

***Found %: C 65.3, 65.4; H 12.9, 13.0. $C_{11}H_{26}SiO$. Calculated %: C 65.3; H 12.9.

EXPERIMENTAL

The trialkylsilanes were prepared by the Grignard method from $HSiCl_3$, CH_3SiHCl_2 and the appropriate alkyl halides. The constants and yields of the three trialkylsilanes are given in Table 5.

TABLE 5

Formula of trialkylsilane*	Boiling point	d_4^{20}	n_D^{20}	Yield (in %)
$CH_3(C_2H_5)_2SiH$	77.9°	0.7054	1.3984	41
$CH_3(n.\text{-}C_3H_7)_2SiH$	128.2	0.7337	1.4135	70
$CH_3(n.\text{-}C_4H_9)_2SiH$	172.9	0.7539	1.4242	72

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*Data for $(C_2H_5)SiH$ was given previously [1]. The alcohols used in the reactions were distilled over metallic calcium and their constants agreed with literature data [2].

The zinc, cadmium, tin and copper chlorides were first dehydrated by the generally accepted procedure [3].

The procedures for synthesizing the trialkylalkoxysilanes and determining their physical constants and silicon contents were described by us previously [1]. The carbon and hydrogen in R_3SiOR were determined by combustion of microsamples of the material in an empty tube.*

As an example of the general procedure of trialkylalkoxysilane synthesis, the preparation of triethylmethoxysilane is presented below.

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*The C and H contents were determined by Iu.N. Platonov, to whom the authors are grateful.

Triethylmethoxysilane. 6.5 g of methyl alcohol, 1.0 g of $ZnCl_2$ and 11.6 g of triethylsilane were boiled until the evolution of hydrogen ceased completely. The reaction was performed at 120-125°. When the reaction had proceeded for 61 hours, 2.4 liters of hydrogen had been evolved. The maximum temperature of the reaction mixture reached 135° at the end of the reaction. Distillation of the reaction mixture yielded 3.2 g of methyl alcohol and 14.2 g of triethylmethoxysilane.

SUMMARY

1. A study was made of the reaction of trialkylsilanes with monohydric alcohols in the presence of metal chlorides.

2. It was shown that some metal chlorides catalyze the dehydrocondensation of R_3SiH with alcohols. The most effective catalysts are $SnCl_2$ and $ZnCl_2$. The yields of trialkylalkoxysilanes reached 99%.

3. A relation was established between the course of the reaction and the structure of R_3SiH and the alcohol, and the nature and amount of the catalyst.

4. Seven new trialkylalkoxysilanes were prepared.

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CATALYTIC DEHYDROCONDENSATION OF TRIALKYLSILANES WITH GLYCOLS

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We previously investigated the catalytic dehydrocondensation of trialkylsilanes with monohydric alcohols. A relation was established between the course of the reaction and the structure of the alcohol and the trialkylsilane and the nature of the alkali metal alcoholate added as a catalyst. It was shown that it was possible to replace the hydrogen atom attached to the silicon by primary, secondary and tertiary alkoxy groups [1].

The present paper reports the catalytic dehydrocondensation of trialkylsilanes with glycols.

Existing literature data show that it is possible to react glycols with $SiCl_4$ and alkyl(aryl) silane chlorides. Thus, dimethyldichlorosilane and ethylene glycol condense to a dimer and other glycols to monomeric dimethylalkylidenedioxysilanes [2]. Sprung and Nelson [3] prepared trimethylsilyl derivatives from trimethylchlorosilane and glycols. Trimethylchlorosilane and $SiCl_4$ with 1,4-butanediol in dioxane, and without it, formed only linear and cross-linked polymers [4]. Hahn [5, 6] treated 1,3- and 1,4-butanediols and diglycol with $SiCl_4$ to isolate monomers with 6, 7 and 8-membered rings. There is no mention of the direct reaction of trialkylsilanes with glycols in the literature.

In studying the catalytic dehydrocondensation of R_3SiH with glycols, we started from $(C_2H_5)_3SiH$, $(C_3H_7)_3SiH$, $(C_4H_9)_3SiH$ and $C_2H_5(C_4H_9)_2SiH$. The dihydric alcohols used were ethylene glycol, 1,2-propanediol, 1,3-, 1,4- and 2,3-butanediol and ethylene diglycol.

As with monohydric alcohols, the glycols did not react with the trialkylsilanes without a catalyst. When heated in a quartz vessel at normal pressure for 100 hours, a mixture of triethylsilane and 1,4-butanediol did not react. In the presence of catalysts (traces of alkali metal glycolates) trialkylsilanes reacted with glycols by the general scheme

$$2R_3SiH + C_nH_{2n}(OH)_2 \xrightarrow{C_nH_{2n}(OM)_2} C_nH_{2n}(OSiR_3)_2 + 2H_2.$$

where $M = Li, Na, K$.

The molar ratio of trialkylsilane, glycol and alkali metal was kept constant in all the experiments (0.15 : : 0.05 : 0.005). The criterion for completion of the reaction was the evolution of the calculated amount of hydrogen.

The advantages of this method of preparing di(trialkylsiloxy)alkanes, in contrast to the synthesis through alkylchlorosilanes, include not only the simplicity of the procedure, but the high yields and the purity of the products formed.

The catalytic dehydrocondensation of R_3SiH with glycols was investigated under the conditions which we normally use and at 160 and 180° in a thermostat. It was established that the reaction proceeded more rapidly at 180° than at 160°. The reaction rate depended on the structure of the glycol and of the trialkylsilane. When the length of the alkyl radicals in R_3SiH was increased, the reaction rate decreased (Table 1).

The calculated values of the activation energy for the reaction of 1,4-butanediol with various trialkylsilanes also confirmed this hypothesis. For example, the activation energy (in kcal/mole) for the formation of 1,4-di-(triethylsiloxy)butane equaled 32.46, for 1,4-di(tripropylsiloxy)butane, 35.52, for 1,4-di(tributylsiloxy)butane, 36.94 and for 1,4-di(ethyldibutylsiloxy)butane, 35.51.

TABLE 1

Formula of trialkylsilane	Reaction time (in minutes)					
	1,4-butanediol		1,3-butanediol		2,3-butanediol	
	160°	180°	160°	180°	160°	180°
$(C_2H_5)_3SiH$	90	75	18	15	140	20
$C_2H_5(C_4H_9)_2SiH$	115	110	30	25	150	55
$(C_4H_9)_3SiH$	320	210	60	35	170	65

The structure of the glycol had a considerable effect on the reaction rate. Ethylene glycol reacted considerably more slowly than 1,4-butanediol and ethylene diglycol. Diprimary butanediol reacted more slowly than disecondary and secondary-primary, more rapidly than the other isomeric glycols (Tables 1 and 2).

TABLE 2

Reaction of Trialkylsilanes with Glycols*

Starting reagents		Reaction time (in minutes)	Reaction product yield (in %)
trialkylsilane	glycol		
$(C_2H_5)_3SiH$	$HO(CH_2)_4OH$	165	74.5
$(C_2H_5)_3SiH$	$HO(CH_2)_2CHOHCH_3$	30	73.1
$(C_2H_5)_3SiH$	$CH_3(CHOH)_2CH_3$	105	74.3
$(C_2H_5)_3SiH$	$HOCH_2CHOHCH_3$	110	81.6
$(C_3H_7)_3SiH$	$HO(CH_2)_4OH$	148	84.3
$(C_3H_7)_3SiH$	$HO(CH_2)CHOHCH_3$	14	87.9
$(C_3H_7)_3SiH$	$CH_3(CHOH)_2CH_3$	26	88.5
$(C_4H_9)_3SiH$	$HO(CH_2)_4OH$	20	85.4
$(C_4H_9)_3SiH$	$HO(CH_2)_2CHOHCH_3$	17	87.5
$(C_4H_9)_3SiH$	$CH_3(CHOH)_2CH_3$	20	83.2
$C_2H_5(C_4H_9)_2SiH$	$HO(CH_2)_4OH$	75	97.6
$C_2H_5(C_4H_9)_2SiH$	$HO(CH_2)_2CHOHCH_3$	5	75.9
$C_2H_5(C_4H_9)_2SiH$	$CH_3(CHOH)_2CH_3$	15	72.1
$C_2H_5(C_4H_9)_2SiH$	$HOCH_2CHOHCH_3$	60	88.5
$C_2H_5(C_4H_9)_2SiH$	$HOCH_2CHOHCH_3$ **	150	82.1
$C_2H_5(C_4H_9)_2SiH$	$HOCH_2CHOHCH_3$ ***	3780	66.3
$C_2H_5(C_4H_9)_2SiH$	$HO(CH_2)_2OH$	560	89.3
$C_2H_5(C_4H_9)_2SiH$	$HO(CH_2)_2O(CH_2)_2OH$	40	88.7

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*The experiments were performed at the boiling point of the mixture. The catalyst was potassium glycolate.

**Catalyst – sodium glycolate.

***Catalyst – lithium glycolate.

As in the case of monohydric alcohols [1], the reaction of R_3SiH with glycols was affected by the nature of the alkali metal used in the catalyst. With an increase in the atomic number of the alkali metal (from lithium to potassium), the reaction rate increased (Table 2). The alcoholates or glycolates, formed in small amounts, played the part of basic catalysts.

In analogy with the mechanism of the reaction of R_3SiH with monohydric alcohols [1], one can assume that the reaction of R_3SiH with glycols probably proceeds by an ion-chain mechanism also.

As a result of the work, we synthesized 16 di(trialkylsiloxy)alkanes, which are not described in the literature (Table 3).

EXPERIMENTAL

Starting reagents. a) The trialkylsilanes were prepared by the action of RMgX on $HSiCl_3$ (or $C_2H_5SiCl_2H$). The constants of the first three compounds corresponded with data which we presented previously [1]. Ethyldibutylsilane had the following constants:

TABLE 3

Properties of Di(trialkylsiloxy)alkanes

Name of compound	Boiling point	Pres-sure (mm)	d_4^{20}	n_D^{20}	Molecular weight*		Content (in %)**					
							Si		C		H	
					calc.	found	calc.	found	calc.	found	calc.	found
1,4-Di(triethylsiloxy)butane	203.0°	10	0.8765	1.4397	318.6	315.3, 313.7	17.6	17.4, 17.3	60.3	60.2, 60.5	12.0	12.2, 12.1
1,3-Di(triethylsiloxy)butane	198.0	14	0.8728	1.4388	318.6	311.9, 314.1	17.6	17.4, 17.6	60.3	59.8, 60,1	12.0	11.9, 12.3
2,3-Di(triethylsiloxy)butane	192.5	13	0.8791	1.4410	318.6	316.0, 314.4	17.6	17.5, 17.6	60.3	60.8, 60.7	12.0	12.1, 12.1
1,2-Di(triethylsiloxy)propane	177.5	9.5	0.8754	1.4372	304.6	301.2, 302.8	18.4	18.4, 18.3	59.1	59.5, 59.4	11.9	12.3, 12.1
1,4-Di(tripropylsiloxy)butane	224.0—224.5	3-3.5	0.8635	1.4458	402.8	398.2, 394.3	13.9	13.9, 13.9	65.6	65.2, 63.3	12.5	12.3, 12.1
1,3-Di(tripropylsiloxy)butane	206.5	5	0.8602	1.4435	402.8	396.2, 393.9	13.9	13.9, 14.0	65.6	65.3, 65.4	12.5	12.3, 12.3
2,3-Di(tripropylsiloxy)butane	217.5	8	0.8633	1.4447	402.8	397.2, 392.4	13.9	13.8, 13.9	65.6	65.3, 65.1	12.5	12.3, 12.1
1,4-Di(tributylsiloxy)butane	292.5	17.5	0.8613	1.4507	486.9	482.7, 484.0	11.5	11.5, 11.2	69.0	68.8, 68.5	12.6	12.4, 12.3
1,3-Di(tributylsiloxy)butane	290.0—290.5	15—16	0.8579	1.4490	486.9	483.1, 481.7	11.5	11.0, 11.2	69.0	69.2, 69.5	12.6	12.7, 12.5
2,3-Di(tributylsiloxy)butane	272.0—272.5	21—22	0.8581	1.4491	486.9	481.8, 485.2	11.5	11.2, 11.2	69.0	68.9, 69.2	12.6	12.3, 12.7
1,4-Di(ethyldibutylsiloxy)butane	205.0—205.3	3.5	0.8672	1.4480	430.8	427.8, 428.2	13.0	12.7, 12.5	66.9	66.4, 66.8	12.6	12.8, 12.7
1,3-Di(ethyldibutylsiloxy)butane	195.0—195.5	3.5-4	0.8652	1.4474	430.8	426.5, 425.9	13.0	12.9, 12.9	66.9	66.5, 67.0	12.6	13.0, 12.7
2,3-Di(ethyldibutylsiloxy)butane	245.5	12	0.8647	1.4474	430.8	427.8, 426.9	13.0	12.6, 12.8	66.9	64.9, 65.7	12.6	12.7, 12.8
1,2-Di(ethyldibutylsiloxy)propane	191.0—192.0	4.5-5.5	0.8677	1.4460	416.8	412.7, 413.3	13.5	13.4, 13.4	66.3	66.4, 66.7	12.6	12.6, 12.7
1,2-Di(ethyldibutylsiloxy)ethane	220.8—221.3	4—5	0.8687	1.4488	402.8	396.3, 398.5	13.9	13.7, 13.6	65.6	64.8, 63.9	12.5	12.6, 12.5
1,5-Di(ethyldibutylsiloxy)-3-oxapentane	292.1	2.5	0.8889	1.4502	446.8	443.5, 444.8	12.6	12.4, 12.3	64.5	63.9, 64.1	12.2	12.3, 12.4

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*The molecular weight was determined cryoscopically in benzene.

**The authors are very grateful to Iu.N. Platonov, who performed the microanalytical determinations.

B.p. 194.0-194.5° (760.9 mm), n^{20}_D 1.4318, d^{20}_4 0.7666, MR_D 58.30; calc. 58.35.

b) The glycols were frozen at a temperature of minus 60-70°, separated from the water, boiled for 1-2 hours over metallic calcium and distilled 3-7 times over fresh portions of metallic calcium. The physical constants of the purified glycols corresponded with literature data [7, 8].

c) Lithium, sodium and potassium were chemically pure reagents.

Procedure. The dehydrocondensation of trialkylsilanes with glycols was performed in two ways.

A. At the boiling point of the mixture. As an example we will describe the synthesis of 1,2-di(ethyldibutylsiloxy)propane.

0.03 g of lithium was dissolved in 3.8 g of 1,2-propanediol, while cooled in a mixture of ice and salt. The lithium glycolate obtained was added to 25.8 g of ethyldibutylsilane. The mixture was boiled for 63 hours. The temperature of the reaction mixture reached 188° at the end of the reaction. 2.5 liters of hydrogen was evolved. The reaction mixture was vacuum distilled to give unchanged ethyldibutylsilane and 13.8 g (66.3%) of 1,2-di-(ethyldibutylsiloxy)propane with b.p. 188.5-189° (2.5-3 mm).

In all cases the distillate consisted of two components – di(trialkylsiloxy)alkane and unchanged trialkylsilane. The difference in the boiling points of the components was 100-150°, which simplified the problem of isolating the product in a satisfactorily pure form.

TABLE 4

v_t	Glycol reacted (mole %)	v_0	Time (min)	Reaction rate
14.8	20.1	13.5	5	2.71
19.9	27.2	18.3	10	1.83
28.3	38.5	25.9	20	1.29
35.7	48.6	32.6	30	1.08
56.2	76.4	51.3	60	0.86
69.2	94.0	63.2	90	0.73
72.2	98.0	66.0	180	0.36

E = 32.46 kcal/mole

B. In thermostats at 160 and 180°. Flasks with two arms were used for these experiments. In one arm was placed a sample of the glycol, with the alkali metal dissolved in it, and in the other, the trialkylsilane. The flask was connected to a 100-ml gas burette through a reflux condenser. The system was placed in a Heppler ultrathermostat filled with distilled dibutyl phthalate. The system was kept at the given temperature for ten minutes. The air was expelled and the reagents mixed. The hydrogen evolved was read off every 5-10 minutes. From these data graphs were plotted of reaction rate against time and the apparent activation energy calculated by the formula

$$E = \frac{2.3 \cdot R \lg \frac{k_1}{k_2} T_1 \cdot T_2}{T_1 - T_2},$$

where k is replaced by the amount of hydrogen evolved in the same time intervals and T_1 and T_2 are the absolute temperatures.

The data from two experiments at 160 and 180° are given below.

Triethylsilane and 1,4-butanediol (Table 4). We used 0.1351 g of 1,4-butanediol, 0.0079 g of potassium and 1.7918 g of $(C_2H_5)_3SiH$. The temperature in the thermostat was 160°. The temperature in the surrounding air was 21.0°. The atmospheric pressure was 769.22 mm and P_0 750.52 mm. The correction factor F = 0.9168. V_t was the volume of hydrogen liberated.

TABLE 5

V_t	Glycol reacted (mole %)	V_0	Time (min)	Reaction rate
23.0	35.5	20.7	2	10.3
26.0	40.9	23.4	3	7.8
28.0	43.2	25.2	4	6.3
29.5	45.7	26.6	5	5.3
33.4	51.7	30.1	10	3.0
38.0	58.9	34.3	15	2.3
39.5	61.2	35.6	20	1.7
42.0	65.2	37.9	30	1.2
44.5	69.0	40.1	40	1.0
51.0	79.0	46.0	60	0.76
54.0	83.8	48.7	75	0.65
69.0	90.0	62.4	140	0.45

E = 32.46 kcal/mole

Triethylsilane and 1,4-butanediol (Table 5). We used 0.1204 g of 1,4-butanediol, 0.0076 g of potassium and 2.6497 g of triethylsilane. The temperature in the thermostat was 180°. The temperature in the surrounding air was 23.0°. The atmospheric pressure was 764.3 mm and P_0 743.2 mm. The correction factor F = 0.9017. V_t was the volume of hydrogen liberated.

SUMMARY

1. A study was made of the catalytic dehydrocondensation of trialkylsilanes with glycols in the presence of lithium, sodium and potassium glycolates. The reaction is a simple and convenient method of synthesizing di(trialkylsiloxy)alkanes, which are formed in 80-90% yield.

2. We synthesized 16 di(trialkylsiloxy)alkanes which are not described in the literature.

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THE MECHANISM OF ACID OXIDATION BY MOLECULAR OXYGEN IN AN n-HEPTANE MEDIUM

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There are several papers in the literature on the oxidation of individual acids by bound oxygen or atmospheric oxygen in the presence of catalysts. The main products of the oxidation of propionic acid [1] with an alkaline potassium permanganate solution were oxalic acid and carbon dioxide. Oxidation of this acid with potassium bichromate in an acid medium gave mainly acetic acid and carbon dioxide. When oxidized with hydrogen peroxide, butyric acid [2] gave a whole series of products: acetic acid, carbon dioxide, acetone, ethyl alcohol and propionaldehyde. Kern [3] and Paquot and de Goursac [4] found methyl ketones in acid oxidation products. It is interesting to note that on oxidizing higher aliphatic acids with an even number of carbon atoms, with atmospheric oxygen in the presence of catalysts, the latter authors detected lower monocarboxylic acids with an even number of carbon atoms, as well as oxalic acid, in the reaction products.

It can be seen from this brief summary that the mechanism of acid oxidation depends on the conditions under which the experiments are carried out. Consequently, the rules governing the oxidation of individual acids in the presence of catalysts with different oxidizing agents cannot be generalized to cover the case of acid oxidation in a medium of an oxidizable hydrocarbon.

Therefore, it is interesting to study the oxidation of acids in a medium of an oxidizable hydrocarbon and by comparing the results with literature data, to try to find the basic characteristics of the oxidation mechanism in relation to the reactions' character and the molecular structure of the acids. Since acids are not only consumed but also formed during the reaction as a result of hydrocarbon oxidation, the most convenient method for solving this problem was to use labeled atoms.

In this investigation on acid oxidation we selected a simple system, which facilitated the analytical part of the work: we studied the oxidation of n-butyric and n-valeric acids in an n-heptane medium. In order to follow the behavior of both the functional group and the carbon chain of the acids, we synthesized n-butyric acid, labeled with radiocarbon in the carboxyl group and n-valeric acid, labeled in the α-position. In addition, we synthesized acetic acid, labeled in the carboxyl group so as to check its oxidizability under the given conditions.

To follow the behavior of the carboxyl group in the oxidized acid, the oxidation of n-heptane, with carboxyl-labeled n-butyric acid added, was carried out. We set up an activity balance for a two-hour experiment at 160° and 6 atm pressure and for a three-hour experiment at 180° and 8 atm pressure. The experimental results are given in the Table. The balance was set up with an accuracy of 2-3%. As the data in the Table show, of the oxidation products only the acid and the carbon dioxide were found to be active. The ketones were inactive. The balance indicated that within the limits of accuracy of the analysis, no other active reaction products were formed or they were unstable under the experimental conditions and were oxidized to carbon dioxide. It should be noted that the only gaseous labeled product was carbon dioxide.

The problem of the oxidizability of acetic acid under the given conditions was solved in the same way. n-Heptane with the addition of 0.02 mmole/ml of acetic acid, labeled in the carboxyl group, was oxidized for four hours. In this case as well, the only active reaction products were acid and carbon dioxide. About 0.1% of the activity was found in the carbon dioxide. Consequently, one may consider that under the experimental conditions the acetic acid was not appreciably decarboxylated.

An investigation of the oxidation of an acid labeled with radiocarbon in the carboxyl group does not make it possible to establish the reactions of the rest of the molecule after decarboxylation. In order to solve this

	Activity (counts/min) in experiments with acid added		
	n-butyric		acetic
	160°, 6 atm, 2 hr	180°, 8 atm, 3 hr	160°, 6 atm, 4 hr
Activity of acids from the experiment	23100	18200	Not determined quantitatively
Activity of CO_2 evolved	724	6760	$1.48 \cdot 10^4$
Ketone activity	–	–	–
Total	23824	24960	
Activity introduced	24400	24400	$1.32 \cdot 10^7$

problem we set up experiments with n-heptane to which n-valeric acid, labeled with radiocarbon in the α-methyl group, was added. The oxidation was carried out at 160° and 6 atm pressure. Of the reaction products, the acids, ketones and carbon dioxide were found to be active. The iodoform and acids formed in an iodoform reaction with the ketones were analyzed for activity content. The iodoform was found to be active and the acids inactive. Therefore, the α-methyl group was active in the ketones.

Due to the small amount of activity, introduced in the form of n-valeric acid and the small absolute amounts of acids which may be separated with paper chromatography, we have not yet been able to establish which of the individual acids, besides valeric acid, were active.

A series of conclusions may be drawn on the mechanism of acid oxidation from the experimental data obtained.

As has already been noted, on oxidizing butyric acid labeled with radiocarbon in the carboxyl group, all the activity was found to be in the acids and carbon dioxide. The activity balance set up indicated that quantitative oxidative decarboxylation occurred. The only gaseous reaction product was carbon dioxide. This experimental fact made it possible to follow the behavior of the acid's carboxyl group in any complex system of hydrocarbon oxidation products.

The reactions of the acid residue after decarboxylation may be established from the experimental data on the oxidation of n-valeric acid labeled in the α-position. The methyl ketone (labeled in the α-methyl group) found in the reaction products made it possible to determine unequivocally the position where the oxidizing agent attacked the acid molecule. The methyl ketone with a labeled α-methyl group may be formed from valeric acid, labeled in the α-position, only by the oxidizing agent attacking the acid's β-methylene group. Consequently, the following reaction took place: $CH_3CH_2CH_2C^{14}OOH \rightarrow CH_3CH_2COC^{14}H_3 + H_2O + CO_2$. Methyl ethyl ketone, carbon dioxide and water were formed.

The most reactive position in an acid molecule in the case of its oxidation is the β-CH_2 group, although the weakest C–H bond is at the α-CH_2 group (due to the effect of the adjacent carboxyl group).

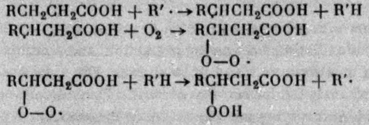
Oxidation of hydrocarbons with atmospheric oxygen is a radical-chain type of reaction with degenerate branching. Apparently, in such reactions the direction of attack of the oxidizing agent is different from the case of an ionic or molecular type of reaction. In fact, as Kharasch [9] showed, in chlorinating acids the main direction of attack by the chlorination agent changes, depending on the type of reaction. In the case of an ionic mechanism, hydrogen substitution occurs mainly at the α-carbon atom while in the case of a radical one – at the β-carbon atom.

Thus, an important factor affecting the direction of the reaction is the type of mechanism by which it proceeds, together with the nature and structure of the oxidizing agent. This hypothesis is confirmed by a series of other literature data. Certain characteristics of the oxidation of acids by hydrogen peroxide are such that the reaction may be considered a radical-chain type of reaction. There is, therefore, reason to consider that the general picture of oxidation would be similar to ours. In fact, by oxidizing n-butyric acid, labeled with radiocarbon in the carboxyl and the β-CH_2 group simultaneously [2], it was shown that the direction of attack of the oxidizing agent was mainly at the β-CH_2 group.

Of course, one cannot exclude an attack by the radical particle on other carbon atoms, although this is less probable. Regrettably, the experimental data available do not permit a determination of the ratios of these directions in oxidation reactions in the total balance of acid conversions in the oxidizable hydrocarbon medium.

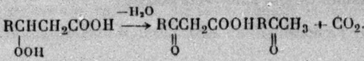
These peculiarities of acid oxidation may be explained from the point of view of electronic concepts. As a carboxyl is an electron-acceptor group and the oxidizing agent is electrophilic, the most convenient position for attack in the acid molecule is the β-methylene group, where the electron density is higher than in the α-position. This explains the difficulty of oxidizing acetic acid in an n-heptane medium with atmospheric oxygen. As this reaction is of a radical type and the acetic acid does not have a β-methylene group, it must be inert to the oxidizing agent — the radical.

Bearing all these considerations in mind, we may give the mechanism developed for the first stage of acid oxidation in the medium of an oxidizable hydrocarbon (R' is any radical system).



$$\mathrm{RCH_2CH_2COOH} + \mathrm{R'}\cdot \rightarrow \mathrm{R}\underset{\cdot}{\mathrm{C}}\mathrm{HCH_2COOH} + \mathrm{R'H}$$
$$\mathrm{R}\underset{\cdot}{\mathrm{C}}\mathrm{HCH_2COOH} + \mathrm{O_2} \rightarrow \mathrm{R}\underset{\substack{|\\ \mathrm{O{-}O}\cdot}}{\mathrm{C}}\mathrm{HCH_2COOH}$$
$$\mathrm{R}\underset{\substack{|\\ \mathrm{O{-}O}\cdot}}{\mathrm{C}}\mathrm{HCH_2COOH} + \mathrm{R'H} \rightarrow \mathrm{R}\underset{\substack{|\\ \mathrm{OOH}}}{\mathrm{C}}\mathrm{HCH_2COOH} + \mathrm{R'}\cdot$$

As yet we can say nothing on the mechanism of the decomposition of hydroperoxides of this type. Only the final reaction products are known and the formation of these may be explained by the following reactions:



$$\mathrm{R}\underset{\substack{|\\ \mathrm{OOH}}}{\mathrm{C}}\mathrm{HCH_2COOH} \xrightarrow{-\mathrm{H_2O}} \mathrm{R}\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}}\mathrm{CH_2COOH}\,\mathrm{R}\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}}\mathrm{CH_3} + \mathrm{CO_2}.$$

EXPERIMENTAL

We carboxylated the Grignard reagents in an apparatus described previously [5]. The acids formed were isolated and stored as the sodium salts and the free acids were prepared from these as required.

Two methods of synthesizing acids labeled in the α-CH_2 group are described in the literature [6]. We chose a slightly different method for the synthesis of n-valeric acid:

$$\mathrm{CH_3CH_2CH_2C^{14}OOH} \xrightarrow{\mathrm{LiAlH_4}} \mathrm{CH_3CH_2CH_2C^{14}H_2OH} \xrightarrow{\mathrm{HBr}} \mathrm{CH_3CH_2CH_2C^{14}H_2Br} \xrightarrow{\mathrm{Mg,CO_2}}$$
$$\rightarrow \mathrm{CH_3CH_2CH_2C^{14}H_2COOH}$$

Butyric acid, labeled in the carboxyl group, was reduced with excess lithium aluminum hydride in ether solution to give n-butyl alcohol in 60% yield [7]. The unreacted, excess lithium aluminum hydride was decomposed with water since decomposition with dilute acid involved considerable unavoidable losses during subsequent washing of the ether solution with water and soda. The ether layer was dried with sodium sulfate and, after evaporation, the n-butyl alcohol was distilled. The radioactive alcohol was converted into the bromide in 70% yield. The bromide gave an 80% yield of labeled n-valeric acid by the procedure described above. The molecular weight of the valeric acid synthesized was 104 (calculated 102). Chromatography of the labeled acid on paper showed that no other acids were present. The over-all yield on CO_2, including the preparation of carboxyl-labeled butyric acid, was 23%.

The oxidation of n-heptane with labeled acids added was performed in the apparatus described previously [8]. For the oxidation we used standard n-heptane, distilled on a column with an efficiency of 20 theoretical plates (b.p. 97.7-97.8°, n_D^{20} 1.3882). 0.02-0.197 mmoles of the appropriate acid was added per ml of n-heptane. The experiments were performed at 160° and a pressure of 6 atm, with oxygen-enriched air (60% O_2) passed through at 2 ml/min.ml. Under these conditions, a second (aqueous acid) layer appeared after two hours oxidation.

The carbon dioxide evolved was absorbed in barium hydroxide solution of known concentration. The barium carbonate precipitate was analyzed for activity. At the end of the experiment, the oxidation mixture was saponified with 1 N alkali in alcohol, then all the neutral reaction products were steam distilled from the alkaline medium, the mixture acidified with sulfuric acid (25%) to congo red and the volatile fatty acids steam distilled off. The total amount of acid was determined by titration with limewater. The aqueous solution of calcium salts was evaporated to dryness in an atmosphere free from carbon dioxide. The amount of acid, determined in this way agreed, within the limits of error, with the total free and bound acid determined by direct titration of an oxidized sample and saponification of the esters in it. This indicated the absence of appreciable amounts of keto- and hydroxyacids and dibasic acids, which did not steam distil. The ketones were precipitated from the neutral fraction as the 2,4-dinitrophenylhydrazones. The activity of the ketones and acids was determined by the procedure published previously [8]. The neutral fraction of the oxidation products was also analyzed for methyl ketones by the iodoform reaction. The iodoform and acids formed were analyzed for activity content. After the iodoform reaction, the acids were isolated in the following way: the alkaline solution was filtered free from iodoform and acidified with sulfuric acid. The iodine liberated was bound with silver sulfate. The solution was made alkaline, the neutral products steam distilled off, the residue made acid to congo with sulfuric acid and the acids steam distilled off.

SUMMARY

1. When oxidized in the medium of an oxidizable hydrocarbon, acids undergo quantitative decarboxylation. If the carboxyl group is labeled with radiocarbon, the only active gaseous reaction product is carbon dioxide. From the activity of the carbon dioxide gas, one may determine the behavior of the carboxyl group of the acid in any complex system of hydrocarbon oxidation products.

2. The oxidizing agent attacks the acid molecule at the β-carbon atom. As a result of decarboxylation of the acid, a methyl ketone is formed with one less carbon atom than the acid.

3. The oxidizability of an acid under the given conditions depends on its molecular structure. An acid of normal structure, without a β-methylene group, is oxidized with considerably more difficulty. Acetic acid is practically inert.

4. n-Valeric acid, labeled in the α-position with radiocarbon, was prepared in 23% yield.

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THERMOCATALYTIC CONVERSIONS OF α-METHYLNAPHTHALENE

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The high-temperature decomposition of alkylnaphthalenes is of interest in connection with the study of the chemism of hydrocarbon cracking [1].

Low-temperature conversions of alkylnaphthalenes in the presence of activated clays demonstrated a series of extremely interesting reactions of this class of hydrocarbon, which are directly related to the conversions of petroleum in nature [2, 3]. These reactions were also studied using α-methylnaphthalene.

Fraction	Temperature		Weight (in g)	d_4^{20}	n_D^{20}	Molecular weight	Melting point of picrate
	boiling point	melting point					
Naphthalene	217—220°	80°	86.3	—	—	—	—
β-Methylnaphthalene	240—242	—	58.0	0.890	1.6049	140.5	113—114°"
α-Methylnaphthalene	243—245	—	105.3	1.0112	1.6148	139.5	140.5
Dimethylnaphthalene	262—265	—	29.3	1.0064	1.6069	155.7	113
Dinaphthyl	190—220 (3 mm)	185.5	34.2	—	—	257	—
Residue	—	—	31.7	—	—	—	—
Coke on catalyst	—	—	37.2	—	—	—	—
Losses	—	—	18.0	—	—	—	—

400 g of the starting hydrocarbon (b.p. 244.7°, d_4^{20} 1.0112, n_D^{20} 1.6150) and an equal amount of activated clay (gumbrine) were heated in an autoclave at 350° for eight hours. The pressure reached 31 atm. At the end of the experiment, 8 m^3 of gas was collected and this had a specific gravity of 0.000723 g/cc (composition in % CO_2 0.49, C_nH_m 0.20, O_2 1.24, CO 0.44, H_2 17.09, CH_4 76, N_2 4.54).

The liquid catalyzate, together with the catalyst, was extracted with benzene. When the solvent had been removed, the fractions shown in the Table were separated by distillation.

The percent conversion of the starting α-methylnaphthalene during the experiment was 69.2.

The β-methylnaphthalene fraction was oxidized with 5% nitric acid. The β-naphthoic acid formed was filtered off and had m.p. 180.5° after recrystallization from ether.

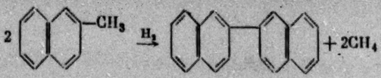
Thus, methane, naphthalene, β-methylnaphthalene, dimethylnaphthalene and dinaphthyl were formed during the experiment.

The formation of naphthalene and dimethylnaphthalene must be normal for these reaction conditions:

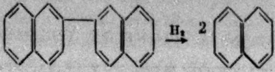
$$2C_{10}H_7CH_3 \rightarrow C_{10}H_8 + C_{10}H_6(CH_3)_2.$$

The formation of the β-isomer may be explained by its greater stability under the experimental conditions.

The result which is specific for this class of hydrocarbon is the internal hydrogenation to form methane and dinaphthyl.



The smaller amount of methane in the products of the experiment in comparison with the dinaphthyl may be explained by the reaction:



The source of hydrogen for the latter reactions may be both the heavy residues, which are impoverished in hydrogen and consist of highly condensed aromatic hydrocarbons, and hydrogen of the catalyst, introduced during its activation.

SUMMARY

1. During the conversion of α-methylnaphthalene on a natural aluminosilicate, an internal hydrogenation reaction, leading to the formation of methane and dinaphthyl was observed in addition to the simple transposition of unchanged aliphatic radicals, which is characteristic of alkylaromatic hydrocarbons.

2. The results of the experiments confirmed the mechanism of the processes of petroleum conversion in the bowels of the earth, which include, on the one hand, simplification of the composition of the petroleum material to methane and, on the other, its elaboration to form highly condensed hydrocarbons.

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SOME CONSIDERATIONS ON THE MECHANISM OF THE FORMATION OF MERCURYAROMATIC COMPOUNDS BY THE OXIDATION OF ARYLHYDRAZINES WITH MERCURIC SALTS

A.B. Bruker and B.B. Levin

A.N. Nesmeianov prepared arylmercuric chlorides by decomposing the binary compounds of aryldiazonium chloride and mercuric chloride with copper powder in organic solvents [1].

$$ArN_2Cl \cdot HgCl_2 + 2Cu \rightarrow ArHgCl + N_2 + Cu_2Cl_2$$

Later it was found [2] that when the binary salts of aryldiazonium chloride and mercuric chloride were decomposed with excess copper in the presence of ammonia, fully substituted mercuryaromatic compounds were formed.

$$2C_6H_5N_2Cl \cdot HgCl_2 + 6Cu + 6NH_3 \rightarrow (C_6H_5)_2Hg + 2N_2 + Hg + 6CuCl \cdot NH_3$$

This method was extended to the synthesis of aromatic compounds of other metals by Nesmeianov and his co-workers.

By reacting phenyldiazonium chloride with metallic mercury, Meclure [3] and Waters [4] prepared phenyl mercuric chloride

$$C_6H_5N_2Cl + Hg \rightarrow C_6H_5HgCl + N_2$$

Fischer and Ehrhard [5] isolated diphenylmercury by oxidizing phenylhydrazine with mercuric oxide in ether solution.

Seide, Scherlin and Bras [6] obtained a good yield of phenylmercuric acetate by oxidizing phenylhydrazine with mercuric acetate in an acetic acid medium in the presence of copper and its salt.

In previous papers we described a method of preparing aromatic compounds of antimony and arsenic, which consists of reacting an arylhydrazine with antimony trichloride [7], antimony pentachloride [8] and arsenic trichloride [9] in a hydrochloric acid medium in the presence of cupric chloride and atmospheric oxygen, and proposed a mechanism for this reaction [10].

In the present work, our aim was to define the mechanism of phenylmercuric acetate formation in the reaction proposed in the paper [6].

It was found that when phenylhydrazine hydrochloride was reacted with mercuric chloride in hydrochloric acid in the presence of cupric chloride, phenylmercuric chloride was formed in 43% yield (on mercuric chloride). The process of phenylmercuric chloride formation, starting from phenylhydrazine and mercuric chloride, may be represented in the following way: the mercuric chloride oxidizes the phenylhydrazine hydrochloride to phenyldiazonium chloride, which reacts with another part of the mercuric chloride to give the binary compound $C_6H_5N_2Cl \cdot HgCl_2$. The latter reacts with phenylhydrazine hydrochloride to give phenylmercuric chloride by the scheme:

$$C_6H_5NHNH_2 \cdot HCl + 4HgCl_2 \rightarrow C_6H_5N_2Cl + 2Hg_2Cl_2 + 4HCl$$

$$C_6H_5N_2Cl + HgCl_2 \rightarrow C_6H_5N_2Cl \cdot HgCl_2$$

$$2C_6H_5N_2Cl \cdot HgCl_2 + C_6H_5NHNH_2 \cdot HCl \xrightarrow{CuCl_2} 2C_6H_5HgCl + C_6H_5N_2Cl + 2N_2 + 4HCl$$

In confirmation of this scheme it was shown that when phenylhydrazine hydrochloride was reacted with the binary compound $C_6H_5N_2Cl \cdot HgCl_2$ under the conditions given above, phenylmercuric chloride was formed. Evidently an analogous scheme occurs in the formation of phenylmercuric acetate. Since phenylmercuric chloride is almost insoluble in hydrochloric acid, then it does not form a complex with phenyldiazonium chloride and, due to this,the reaction stops at the formation of phenylmercuric chloride.

EXPERIMENTAL

Reaction of phenylhydrazine hydrochloride and mercuric chloride in hydrochloric acid in the presence of cupric chloride. Phenylhydrazine hydrochloride (14.5 g) and cupric chloride (1 g) were added with stirring to a hydrochloric acid solution of mercuric chloride (27.3 g) in a jar fitted with a stirrer. At the beginning of the reaction, the color of the solution was green. After six hours stirring, the color disappeared and the suspended precipitate settled out. After 14-hours stirring, the solution again acquired a green color. The precipitate was sucked off, washed with water, alcohol and ether and dried in air. When the precipitate was recrystallized from boiling acetone with slow cooling, the acetone solution deposited lustrous scales. When the crystalline product had been washed with alcohol and ether, its weight was 13.5 g (43.1%). The product melted at 248-252°; after a second recrystallization from acetone, the product had m.p. 251-253°. A mixed melting point with phenylmercuric chloride, prepared by another method, was not depressed.

Reaction of phenylhydrazine hydrochloride with the binary compound $C_6H_5N_2Cl \cdot HgCl_2$ in hydrochloric acid in the presence of cupric chloride. A mixture of the binary compound $C_6H_5N_2Cl \cdot HgCl_2$ (30 g), phenylhydrazine hydrochloride (10 g), cupric chloride (0.5 g) and dilute hydrochloric acid (1:2) was stirred for 1.5-2 hours in a jar and the precipitate formed was separated. The reaction was accompanied by vigorous frothing (evolution of nitrogen). Two recrystallizations of the precipitate from ethyl acetate yielded 5.5 g of material (28% on the binary compound). A mixed melting point with phenylmercuric chloride was not depressed.

SUMMARY

It was shown that the reaction of phenylhydrazine hydrochloride and mercuric chloride in hydrochloric acid in the presence of cupric chloride gave phenylmercuric chloride. A reaction scheme is proposed.

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HALOGENATION OF AROMATIC SILANES

VI. PREPARATION AND PROPERTIES OF CHLORO DERIVATIVES OF p-(TRICHLOROMETHYL)PHENYLTRICHLOROSILANE

G.V. Motsarev and A.Ia. Iakubovich

We showed previously [1] that the introduction of an orientant of the first order (a methyl group) into the phenyltrichlorosilane molecule leads to activation of the aromatic nucleus and, for example, p-tolyltrichlorosilane is halogenated considerably more readily than phenyltrichlorosilane. It seemed interesting to determine the effect of introducing orientants of the second order, such as CCl_3 and CF_3 groups, into the phenyltrichlorosilane molecule on its chlorination. With this aim, we studied the chlorination of p-(trichloromethyl)phenyltrichlorosilane and p-(trifluoromethyl)phenyltrifluorosilane. The halogenation of these silanes is not described in the literature.

It is known that the CCl_3 group is a meta-orienting substituent. When $C_6H_5CCl_3$ is chlorinated in the presence of $SbCl_5$ and iodine, the meta-chloro derivative is formed predominantly [2]; nitration of $C_6H_5CCl_3$ to the mononitro derivative gives mainly the meta-nitro isomer [3]. In catalytic chlorination, in contrast to bromination, the $SiCl_3$ group in $C_6H_5SiCl_3$ also acts as a meta-orientant [4].

Considering that meta-orientants passivate the benzene nucleus in substitution reactions, one would expect that the presence of two meta-orienting substituents in the para position of p-(trichloromethyl)phenyltrichlorosilane would lead to strong deactivation of the benzene nucleus.

Actually, p-(trichloromethyl)phenyltrichlorosilane could not be chlorinated in the absence of catalyst when treated with a large excess of chlorine (molar ratio 1 : 22) at 190-220°.

When p-$CCl_3C_6H_4SiCl_3$ was treated with chlorine in the presence of $FeCl_3$, the reaction proceeded with difficulty at 100-110°. Depending on the molar ratio of the reagents, mono- and dichloro-substituted p-(trichloromethyl)phenyltrichlorosilanes were obtained under these conditions in yields of 68.3 and 55.4%. It was not possible to isolate a trichloro derivative from the reaction products even after treating p-$CCl_3C_6H_4SiCl_3$ with excess chlorine for a long time. In this case the main reaction product was p-(trichloromethyl)dichlorophenyltrichlorosilane. It was thus established that together with substitution, destructive chlorination occurs with the formation of $SiCl_4$ and the corresponding chloro-substituted benzotrichlorides.

The chlorination of p-(trichloromethyl)phenyltrichlorosilane may be represented by the following scheme:

$$CCl_3C_6H_4SiCl_3 \xrightarrow[-HCl]{+Cl_2} CCl_3C_6H_3ClSiCl_3 \xrightarrow[-HCl]{+Cl_2} CCl_3C_6H_2Cl_2SiCl_3 \xrightarrow{+Cl_2} CCl_3C_6H_2Cl_3 + SiCl_4$$

Cleavage of the Si−C bond by chlorine in p-$CCl_3C_6H_4SiCl_3$ proceeds more readily than in $C_6H_5SiCl_3$, but with more difficulty than in p-$CH_3C_6H_4SiCl_3$. Thus, while cleavage occurs to a very small degree in the chlorination of $C_6H_5SiCl_3$ in the presence of $FeCl_3$ only at 140-150° [5], in the case of p-$CCl_3C_6H_4SiCl_3$, this reaction occurs at 115-130° and at the same time, destructive chlorination of p-$CH_3C_6H_4SiCl_3$ is observed, even at 90 to 100° [1].

The effect of reagent ratio and temperature on the results of chlorinating p-$CCl_3C_6H_4SiCl_3$ are illustrated by the data presented in the Table.

Effect of Conditions on Product Composition in the Chlorination of p-$CCl_3C_6H_4SiCl_3$

Chlorination conditions			Composition of reaction products			Silane cleaved (in %)
amount of $FeCl_3$ (in %) of weight of silane taken)	temperature	molar ratio of silane to chlorine	unchanged silane (%)	chlorination products		
				total yield (in %)	main reaction product	
1.4	100-110°	1:4.3	12.5	68.3	Monosubstituted	–
1.7	100-110	1:8.7	–	84.4	Disubstituted	–
1.4	115-130	1:22.2	–	70.2	Disubstituted	9.2

The mono- and dichloro derivatives of p-(trichloromethyl)phenyltrichlorosilane were separated and the physicochemical data for them are given (see experimental).

To determine the structure of the monochloro derivative of p-(trichloromethyl)phenyltrichlorosilane synthesized, we planned to use cleavage of it with bromine (after preliminary exhaustive methylation [6]) and oxidation of the cleavage products with chromic acid, leading to the formation of the corresponding chlorobromo derivatives of benzoic acid.

Before using these reactions for this purpose, they were first tested by applying them to unsubstituted p-(trichloromethyl)phenyltrichlorosilane, for which the latter was first methylated using CH_3MgI.

It is known that the reaction of polyhalo derivatives of hydrocarbons with organomagnesium compounds is complicated; parallel with the exchange reaction, a side reaction often occurs in which the radicals formed combine with each other. For example, when $C_6H_5CHCl_2$ is treated with CH_3MgI, the reaction gives, exclusively, dichlorostilbene; under these conditions, $C_6H_5CCl_3$ forms tolan tetrachloride [7].

$$2C_6H_5CHCl_2 + 2CH_3MgI \rightarrow C_6H_5CHClCHClC_6H_5 + C_2H_6 + 2MgICl$$
$$2C_6H_5CCl_3 + 2CH_3MgI \rightarrow C_6H_5CCl_2CCl_2C_6H_5 + C_2H_6 + 2MgICl$$

Considering this, one would expect that the treatment of p-$CCl_3C_6H_4SiCl_3$ with CH_3MgI to prepare the corresponding aryltrimethylsilane could give as the main reaction product, 4,4'-di(trimethylsilyl)tolan tetrachloride.

$$2p\text{-}(Cl_3Si)C_6H_4CCl_3 + 8CH_3MgI \rightarrow (CH_3)_3SiC_6H_4CCl_2CCl_2C_6H_4Si(CH_3)_3 + 8MgICl + C_2H_6$$

However, experiment showed that when p-$CCl_3C_6H_4SiCl_3$ was treated with excess CH_3MgI, 4,4'-di(trimethylsilyl)tolan dichloride was formed and this was isolated in a pure state and characterized.

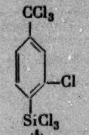
$$2p\text{-}(Cl_3Si)C_6H_4CCl_3 + 10CH_3MgI \rightarrow (CH_3)_3SiC_6H_4CCl{=}CClC_6H_4Si(CH_3)_3 + 10MgICl + 2C_2H_6$$

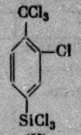
Similarly to other aryltrimethylsilanes, 4,4'-di(trimethylsilyl)tolan dichloride was readily cleaved with bromine at the $C_{arom}-Si$ bond to form $(CH_3)_3SiBr$ and 4,4'-dibromotolan dichloride, which was converted into p-bromobenzoic acid when oxidized with chromic acid.

$$(CH_3)_3SiC_6H_4CCl{=}CClC_6H_4Si(CH_3)_3 + 2Br_2 \rightarrow BrC_6H_4CCl{=}CClC_6H_4Br + 2(CH_3)_3SiBr$$
$$\xrightarrow[H_2SO_4]{+K_2Cr_2O_7} 2p\text{-}BrC_6H_4COOH$$

When a chlorine atom is introduced into p-(trichloromethyl)phenyltrichlorosilane, the two isomers (I) and (II) may be formed and cleavage of these with bromine (after preliminary exhaustive methylation), followed by oxidation of the cleavage products, could lead to the formation of 3-chloro-4-bromo- and 2-chloro-4-bromobenzoic acids (III and IV), respectively (melting points 218 and 166°, respectively).

When monochloro(p-trichloromethyl)phenyltrichlorosilane, obtained by chlorinating p-trichloromethylphenyltrichlorosilane, was treated as described above, we isolated a chlorobromobenzoic acid with m.p. 182-184°. The latter indicated that the acid was not pure and apparently was a mixture of the two possible isomeric acids (III and IV).


(I)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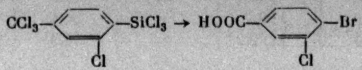
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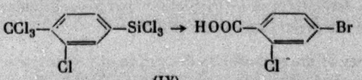
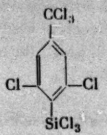

(IV)

From this it follows that the monochloro(p-trichlormethyl)phenyltrichlorosilane was a mixture of the two possible isomers.

As regards the structure of the dichloro derivatives of p-trichloromethylphenyltrichlorosilane isolated, of the four possible isomers (V-VIII), the most probable structures are (V), (VI) and (VIII).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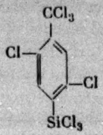
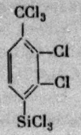
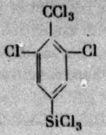

(VI)


(VII)


(VIII)

Thus, as a result of studying the reaction of p-$CCl_3C_6H_4SiCl_3$ with chlorine in the presence of $FeCl_3$, we showed that the entering chlorine atom is oriented by both of the available substituents (1-CCl_3, 4-$SiCl_3$) into positions 2 and 3.

In contrast to p-(trichloromethyl)phenyltrichlorosilane, when p-(trifluoromethyl)phenyltrifluorosilane* was treated with chlorine for a long period at its boiling point (118-119°) in the presence of $FeCl_3$ (1.7%),it was completely unchlorinated. This is apparently the result of strong deactivation of the nucleus by the CF_3 group and the relatively low chlorination temperature.

EXPERIMENTAL

Chlorination of p-trichloromethylphenyltrichlorosilane. A current of dry chlorine was passed at a rate of 20 ml/min for 6 hours 50 minutes through a porous glass plate into a mixture of 28 g of p-(trichloromethyl)phenyltrichlorosilane (m.p. 66-67°)**and 0.4 g of anhydrous $FeCl_3$ in a glass column (220 mm high and 25 mm in diameter) at 100-110°, with a layer 50 mm high in the column. The chlorination proceeded with difficulty and a large amount of chlorine passed through,unchanged. When the reaction mixture had been flushed with air, it had gained 2.6 g (compared with 3.0 g required for chlorination to the monochloro derivative). The chlorination products were distilled in vacuum (13 mm) to give: 1st fraction, b.p. 160-170°, 3.5 g, 2nd fraction, b.p. 170-182°, 24.1 g. The first fraction was mainly unchanged p-(trichloromethyl)phenyltrichlorosilane. Redistillation of the second fraction yielded 21.1 g of liquid with b.p. 171-179° (13 mm), which corresponded to monochloro(p-trichloromethyl)phenyltrichlorosilane in analysis. The yield was 68.3%, calculated on the p-(trichloromethyl)-phenyltrichlorosilane taken for reaction. The colorless, mobile liquid with a sharp smell fumed in air.

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*p-$CF_3C_6H_4SiF_3$ was prepared by fluorinating p-$CCl_3C_6H_4SiCl_3$, using SbF_3 by the method described by Frost [8].

**The p-(trichloromethyl)phenyltrichlorosilane was prepared by liquid-phase, catalytic chlorination of p-tolyltrichlorosilane in the presence of azobisisobutyronitrile [9].

B.p. 172-177° (13 mm) d^{20}_{20} 1.6369, $n^{20}D$ 1.5777.

Found %: C 23.42, 23.27; H 1.03, 0.91; Cl 68.04, 68.21; Si 7.82, 7.97. $C_7H_3Cl_7Si$. Calculated %: C 23.10; H 0.82; Cl 68.36; Si 7.70.

Chlorination of p-(trichloromethyl)phenyltrichlorosilane to the dichloro derivative was carried out similarly under the same conditions, except that the amount of chlorine passed was correspondingly increased. 23 g of p-(trichloromethyl)phenyltrichlorosilane, which was chlorinated for twelve hours (4.3 g increase in weight), yielded 15.4 g of a colorless, mobile (when heated) liquid, which crystallized on cooling to give solid dichloro(p-trichloromethyl)phenyltrichlorosilane (yield 55.4%). Monochloro(p-trichloromethyl)phenyltrichlorosilane (4.5 g) was a side product. The total yield of di- and monochloro derivatives was 84.4%. The dichloro(p-trichloromethyl)phenyltrichlorosilane was a white, crystalline substance (prisms).

B.p. 189-195° (13 mm), m.p. 123-126° (from chloroform).

Found %: C 21.72, 21.61; H 0.62, 0.59; Cl 70.16, 70.94; Si 7.12, 7.21. $C_7H_2Cl_8Si$. Calculated %: C 21.10; H 0.50; Cl 71.3; Si 7.03.

In an attempt to prepare trichloro(p-trichloromethyl)phenyltrichlorosilane by chlorination of 20.9 g of p-(trichloromethyl)phenyltrichlorosilane in the presence of $FeCl_3$ (ten hours at 115-120° and 16 hours at 125-130°, chlorine rate 20 ml/min), the reaction products yielded 1.0 g of $SiCl_4$ and 17.7 g of dichloro(p-trichloromethyl)-phenyltrichlorosilane. The yield was 70.2%. When 10.6 g of p-(trichloromethyl)phenyltrichlorosilane was chlorinated in the absence of catalyst (190-200°, 13 hours and chlorine rate 20 ml/min), the reaction products yielded unchanged starting silane.

Reaction of p-trichloromethylphenyltrichlorosilane with CH_3MgI. To an ether solution of CH_3MgI, prepared from 7.2 g of magnesium, 40.2 g of CH_3I and 100 ml of absolute ether, was added a solution of 15 g of p-trichloromethylphenyltrichlorosilane in 40 ml of ether and the mixture boiled for 30 minutes on a water bath (the reaction mixture separated into two layers) and then decomposed with 5% hydrochloric acid with cooling (0°). After the usual treatment, the ether layer yielded 6.6 g of a solid substance, which corresponded in analysis to 4,4'-di(trimethylsilyl)tolan dichloride. The yield was 67%. The white crystalline substance (lustrous platelets) had m.p. 185-186° (from acetone) and was difficultly soluble in hot alcohol and cold acetone and readily soluble (at normal temperatures) in benzene and chloroform.

Found %: C 60.31, 60.95; H 7.33, 7.36; Cl 17.80, 17.90; Si 13.73, 13.60. $C_{20}H_{26}Cl_2Si_2$. Calculated %: C 61.06; H 6.6; Cl 18.06; Si 14.25.

Cleavage of 4,4'-di(trimethylsilyl)tolan dichloride with bromine. 3.5 g of bromine was added dropwise with stirring over a period of ten minutes to 4 g of 4,4'-di(trimethylsilyl)tolan dichloride. The reaction was accompanied by considerable evolution of heat (the temperature of the mixture reached 90°). When all the bromine had been added, the mixture was heated at 70-80° for 20 minutes and then 2.8 g (90.3%) of $(CH_3)_3SiBr$ with b.p. 78-80° was distilled off from it. After removal of the $(CH_3)_3SiBr$, the solid residue was recrystallized from a mixture of alcohol and acetone. We obtained 3.4 g of white crystals with m.p. 155-157°, which corresponded in analysis to 4,4'-dibromotolan dichloride. The yield was 80.2%.

Found %: C 41.63, 41.44; H 2.07, 2.01; (Cl + Br) 57.41, 57.11. $C_{14}H_8Cl_2Br_2$. Calculated %: C 41.27; H 1.96; (Cl + Br) 56.77.

Oxidation of 4,4'-dibromotolan dichloride. 3.5 ml of concentrated sulfuric acid was added over a period of ten minutes with stirring to a mixture of 2 g of 4,4'-dibromotolan dichloride, 2.5 g of $K_2Cr_2O_7$ and 5 ml of water. At this, the temperature of the mixture rose and a vigorous reaction began. When the sulfuric acid had been added and the evolution of heat ceased, the reaction mixture was boiled gently for 30 minutes. When the reaction mixture had cooled, 25 ml of water was added and the precipitate formed filtered, washed with water (until no longer acid to congo) and dissolved in 5% NaOH solution. The insoluble residue was filtered off and the filtrate poured in a thin stream with stirring into 5% sulfuric acid solution (to a weakly acid reaction). The precipitate formed was filtered off, washed first with a small amount of dilute sulfuric acid and then with water and dried. We obtained 1.34 g (68%) of white crystals with m.p. 250°, which corresponded in analysis to p-bromobenzoic acid. Literature data [10]: m.p. 250-251°.

Found %: Br 40.23, 40.46. $C_7H_5O_2Br$. Calculated %: Br 39.80.

Reaction of monochloro(p-trichloromethyl)phenyltrichlorosilane with CH_3MgI and subsequent treatment of the reaction product with bromine and chromic acid. The experiments were carried out by the procedure described in the previous sections; the intermediate reaction products were not isolated in a pure form. When 5.4 g of monochloro(p-trichloromethyl)phenyltrichlorosilane was treated with CH_3MgI, prepared from 2.65 g of Mg and 13.3 g of CH_3I in ether solution, we obtained 3.0 g of a thick, dark-yellow liquid, which was treated with 2.3 g of bromine and gave 1.5 g of $(CH_3)_3SiBr$ (b.p. 78-80°). After removal of the $(CH_3)_3SiBr$, the residual solid (3 g) was oxidized with chromic acid (4 g of $K_2Cr_2O_7$ + 5.6 ml of conc. H_2SO_4 + 6 ml of water). We obtained ~2 g of white crystals with m.p. 182-184° (from alcohol), which dissolved completely in 5% NaOH solution and corresponded in analysis to chlorobromobenzoic acid.

Found %: (Br + Cl) 49.27, 49.31. $C_7H_4O_2BrCl$. Calculated %: (Br + Cl) 49.04.

SUMMARY

1. Chlorination of $p\text{-}CCl_3C_6H_4SiCl_3$ in the presence of $FeCl_3$ gave mono- and dichloro derivatives. We were unable to obtain derivatives of $p\text{-}CCl_3C_6H_4SiCl_3$ with three and four chlorines in the nucleus (cleavage of the C−Si bond occurred).

2. It was found that the monochloro derivative of $p\text{-}CCl_3C_6H_4SiCl_3$ was a mixture of 2-chloro- and 3-chloro-4-(trichloromethyl)phenyltrichlorosilanes.

3. It was established that $p\text{-}CF_3C_6H_4SiF_3$ does not react with chlorine at its boiling point (118-119°), even in the presence of $FeCl_3$.

4. It was shown that treatment of $p\text{-}CCl_3C_6H_4SiCl_3$ with methylmagnesium iodide yielded 4,4'-di(trimethylsilyl)tolan dichloride.

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REACTION OF β-CHLOROVINYL KETONES WITH β-DICARBONYL COMPOUNDS

VII. ACID CLEAVAGE OF α-ALKYL-α-(3-KETOALKENYL)-ACETOACETIC ESTERS

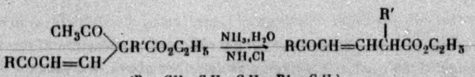
N.K. Kochetkov and B.P. Gottykh

In one of our previous works, together with L.I. Kudriashov, we were able to ketovinylate α-alkylacetoacetic esters to form α-alkyl-α-(3-ketoalkenyl)-acetoacetic esters [1]. The new class of compounds obtained is of undoubted interest for organic synthesis.

We began the investigation of the chemical behavior of α-alkyl-α-(3-ketoalkenyl)-acetoacetic esters with a study of their acid cleavage. The compounds investigated were vinylogs of α,α-diacyl derivatives of aliphatic esters, whose acid cleavage, as is known, leads to the corresponding β-ketoester of this or other structures (depending on the relative ease of elimination of the acyl groups) or a mixture of the two possible β-ketoesters. In our case we naturally expected that the acyl group would be eliminated more readily than the β-ketovinyl group.

Cleavage of α-alkyl-α-(3-ketoalkenyl)-acetoacetic esters by the most general method, i.e., treatment with concentrated alkali solutions, was impossible due to the lability of these compounds and their tendency toward complex condensations. An attempt at cleavage using catalytic amounts of sodium alcoholate by Dieckmann's method [2] gave negative results. When α-alkyl-α-(3-ketoalkenyl)-acetoacetic esters were treated with gaseous ammonia in ether solution, as recommended by Bouveault [3] for the cleavage of diacylacetic esters, the reaction was accompanied by side processes and it was only possible to isolate very small yields of analytically pure acid-cleavage products from the mixture obtained.

The use of aqueous ammonia solution containing ammonium chloride for the cleavage [4] was successful. In this case the α-alkyl-α-(3-ketoalkenyl)-acetoacetic esters underwent fairly smooth acid decomposition to form esters of α-(3-ketoalkenyl)-alkanoic acids.



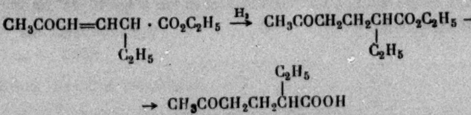
$$\begin{matrix} CH_3CO \\ RCOCH{=}CH \end{matrix}\Big\rangle CR'CO_2C_2H_5 \xrightarrow[NH_4Cl]{NH_3,H_2O} RCOCH{=}CHCH(R')CO_2C_2H_5$$

$(R = CH_3,\ C_2H_5,\ C_3H_7;\ R' = C_2H_5)$.

Detailed investigation of the reaction, using α-ethyl-α-(3-ketobutenyl)-acetoacetic ester, showed that the result depended on the amount of ammonia solution used, as is shown by the data in the Table.

As the data in the Table shows, the optimal concentration of ammonia found is also suitable for performing the reaction on a larger scale. Further investigation showed that the reaction was of a general character. On extending it to other homologs of α-alkyl-α-(3-ketoalkenyl)-acetoacetic esters, it was found that the cleavage became more difficult as the molecular weight of the compound increased and therefore the optimal ammonia concentration had to be found for each case.

The structure of the compounds we obtained was proved on the example of the simplest of them – the ester of α-(3-ketobutenyl)-butyric acid – by the scheme



$$CH_3COCH{=}CHCH(C_2H_5) \cdot CO_2C_2H_5 \xrightarrow{H_2} CH_3COCH_2CH_2CH(C_2H_5)CO_2C_2H_5 \rightarrow CH_3COCH_2CH_2CH(C_2H_5)COOH$$

Cleavage of α-Ethyl-α-(3-ketobutenyl)-acetoacetic Ester

Reagent used				Reaction temperature	Product yield (in %)
ester (in g)	NH_3 (in ml)	NH_4Cl (in g)	H_2O (ml)		
28.2	5	16	75	43-45°	25
28.2	10	16	75	46-50	48
28.2	15	16	75	49-50	70
40.0	21.5	22.6	106	47-48	69

Hydrogenation of the substance over palladium on barium sulfate gave the ester of α-ethyl-δ-ketocaproic acid, which was hydrolyzed to give the acid itself and the latter was identified as the semicarbazone.

The esters of α-(3-ketoalkenyl)-alkanoic acids obtained were vinylogs of α-alkyl-β-ketoacid esters, whose synthesis was recently achieved in our laboratory by cleavage of alkyl-(3-ketoalkenyl)-malonic esters [5]. The reaction described in the present article is a more convenient method of synthesizing them.

EXPERIMENTAL

Ethyl α-(3-ketobutenyl)-butyrate. 16 g of ammonium chloride was dissolved in 75 ml of water, 15 ml of aqueous ammonia solution (d.0.9) added, the solution heated to 45° and added to 28.2 g of α-ethyl-α-(3-ketobutenyl)-acetoacetic ester in a flask fitted with a stirrer, a thermometer and an air condenser. The reaction mixture was stirred vigorously and heated for two minutes on a water bath at 50°. The reaction proceeded with the evolution of heat and the temperature of the mixture was kept within the range 49-50°. After 40 minutes the reaction mass was cooled, the oily layer, containing the bulk of the substance, separated and the aqueous solution extracted with ether (2 x 50 ml). The ether extracts were combined with the bulk of the material, washed with dilute (1:2) hydrochloric acid (2 x 50 ml) and dried over baked magnesium sulfate. After removal of the ether, the residue was vacuum distilled and a fraction with b.p. 89-93° (1 mm) collected. After three distillations the substance had the constants:

B.p. 85-88° (1 mm), d_4^{20} 1.0058, n_D^{20} 1.4560, MR_D 49.79; calc. 49.58.

Found %: C 64.96, 64.92; H 8.78, 8.95. $C_{10}H_{16}O_3$. Calculated %: C 65.19; H 8.75.

The yellowish oil was miscible with organic solvents, insoluble in water and stable during storage. The yield was 16 g (70%).

Ethyl α-(3-ketopenten-1-yl)-butyrate was obtained similarly from 30 g of α-ethyl-α-(3-ketopenten-1-yl)-acetoacetic ester by treatment with 16 g of ammonium chloride in 75 ml of water and 25 ml of aqueous ammonia solution.

In this case the reaction mixture did not evolve heat and the temperature of the reaction mixture was kept for 40 minutes in the range 51-55°. After working up as described above, we vacuum distilled the residue, collecting a fraction with b.p. 93.5-97° (0.5 mm). After three distillations, the substance had the constants:

B.p. 88-91° (1 mm), d_4^{20} 0.9907, n_D^{20} 1.4562, MR_D 54.42; calc. 54.12.

Found %: C 66.34, 66.43; H 9.32, 9.21. $C_{11}H_{18}O_3$. Calculated %: C 66.64; H 9.15.

The yield was 15.7 g (63.5%). The yellowish oil was miscible with organic solvents, insoluble in water and stable during storage.

In a similar experiment, where the concentration of aqueous ammonia used for the cleavage was a factor of 2.5 less and corresponded to the concentration used in the previous experiment, the yield was 20%.

Ethyl α-(3-ketohexen-1-yl)-butyrate was prepared similarly from 31.8 g of α-ethyl-α-(3-ketohexen-1-yl)-acetoacetic ester by treatment with 16 g of ammonium chloride in 75 ml of water and 25 ml of aqueous ammonia solution. The temperature of the reaction mixture was kept in the range 46-48° for ten minutes. Distillation in vacuum yielded a fraction with b.p. 98-100° (1 mm).

After three distillations, the substance had the constants:

B.p. 92-94° (1 mm), d_4^{20} 0.9726, n_D^{20} 1.4561, MR_D 59.30; calc. 58.81.

Found %: C 67.85, 67.89; H 9.68, 9.61. $C_{12}H_{20}O_3$. Calculated %: C 67.89; H 9.50

The yield was 10 g (38%). The yellowish oil was miscible with organic solvents, insoluble in water and stable during storage.

In a similar experiment, where the ammonia concentration was half as great, the yield was 20%.

Ethyl α-ethyl-δ-ketocaproate. 15 g of ethyl α-(3-ketobutenyl)-butyrate was hydrogenated in 50 ml of ether over palladium on barium sulfate. Over a period of four hours, 2090 ml of hydrogen (2000 ml calculated) was consumed. Working up in the usual way gave 14 g of substance with b.p. 63-64° (0.5 mm). After a second distillation the substance had the constants:

B.p. 64-66° (1 mm), d_4^{20} 0.9671, n_D^{20} 1.5293, MR_D 49.68; calc. 50.02.

Found %: C 64.70, 64.62; H 9.83, 9.58. $C_{10}H_{18}O_3$. Calculated %: C 64.48; H 9.75.

The colorless liquid had a characteristic smell.

The semicarbazone formed colorless needles with m.p. 95.5-97° (from 30% ethyl alcohol).

Found %: N 17.47, 17.40. $C_{11}H_{21}O_3N_3$. Calculated %: N 17.27.

α-Ethyl-δ-ketocaproic acid. 9 g of ethyl α-ethyl-δ-ketocaproate was boiled for two hours with a solution of 7.7 g of sodium hydroxide in 23 ml of water. The solution was acidified with hydrochloric acid (1:2) to an acid reaction to congo and extracted with ether and the ether extracts dried over magnesium sulfate. When the solvent had been removed, the residue was vacuum distilled to give a fraction with the following constants:

B.p. 132-133° (1 mm), n_D^{20} 1.4480.

Literature data: b.p. 135-137° (2 mm) [6]; 147° (7 mm), n_D^{20} 1.4483 [5].

The yield was 5.6 g (72.5%).

The semicarbazone was prepared by the usual method.

M.p. 128-130° (from 30% ethyl alcohol).

Found %: N 19.72, 19.54. $C_9H_{17}O_3N_3$. Calculated %: N 19.52.

Literature data: m.p. 127-129° [6], 131-131.5° [5].

SUMMARY

The acid cleavage of α-alkyl-α-(3-ketoalkenyl)-acetoacetic esters was performed with aqueous ammonia solution, containing ammonium chloride. Using this reaction, we developed a general method of synthesizing α-(3-ketoalkenyl)-alkanoic esters. It was shown that with an increase in the molecular weight of the α-alkyl-α-(3-ketoalkenyl)-acetoacetic ester, the acid cleavage required more drastic conditions and gave lower yields of α-(3-ketoalkenyl)-alkanoic esters.

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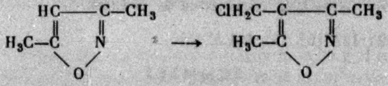
INVESTIGATION IN THE ISOXAZOLE SERIES

VII. CHLOROMETHYLATION OF ISOXAZOLES

N.K. Kochetkov, E.D. Khomutova and M.V. Bazilevskii

In a previous report [1] it was shown that 3-chloromethylisoxazole was a convenient starting material for the synthesis of isoxazole derivatives with various functional substituents in the side chain. In this connection it seemed of great interest to develop a general method for synthesizing other chloromethylisoxazoles and the most suitable method appeared to be the chloromethylation reaction. Despite the fact that this method is applied very widely in the aromatic series, information on the chloromethylation of heterocyclic compounds is extremely scanty and is limited to data on the chloromethylation of some thiophenes [2-4] and esters of pyromucic acid [5, 6]. No information has been published up to now on the chloromethylation of nitrogen-containing heterocyclic compounds, including isoxazoles. An investigation of the chloromethylation of isoxazoles is also of fundamental interest in broadening our knowledge of this interesting heterocyclic system, for which the only electrophilic substitution reactions known are separate, haphazard examples of halogenation [7], nitration [8] and sulfonation [9].

In our laboratory it was recently shown that 3,5-dimethylisoxazole will undergo chloromethylation [10]. In the present report we present data from a detailed study of this reaction for various substituted isoxazoles. We first made a detailed study of chloromethylation conditions using the readily available 3,5-dimethylisoxazole so as to select the most advantageous procedure for chloromethylation in the isoxazole series. The choice of this example was also dictated by the fact that in this case isomer formation was excluded.



3,5-Dimethylisoxazole was chloromethylated with various agents (paraformaldehyde with hydrogen chloride, dichlorodimethyl ether and monochlorodimethyl ether), using various catalysts (zinc chloride, sulfuric acid and stannic chloride) and in various solvents (hydrochloric acid, sulfuric acid, dichloroethane, chloroform and excess chlorodimethyl ether). The results obtained in studying this reaction are presented in Table 1.

As the data in Table 1 show, the result of the reaction depended to a considerable degree on the nature of the chloromethylating agent, the catalyst and the reaction conditions. In most cases a considerable part of the original 3,5-dimethylisoxazole was recovered unchanged (experiments 1, 4 and 7-11). When the reaction temperature was raised to 70-75° or the heating time was increased, there was considerable tar production in the reaction mixture; the yield of chloromethyl derivative was not thus increased, but the original 3,5-dimethylisoxazole could not be recovered from the reaction mixture. The optimal conditions, which we also used in further work, were chloromethylation with paraformaldehyde and hydrogen chloride (experiment 1) in dichloroethane (yield on dimethylisoxazole used, about 30% and 40-45% on that which reacted). Chloromethylation with dichlorodimethyl ether (experiment 4) gave approximately the same results, but this method was less convenient as regards starting materials. The most suitable catalyst was zinc chloride. Sulfuric acid was too drastic and, on the other hand, stannic chloride was too mild a catalyst. The reaction was best performed in dichloroethane or chloroform and the use of excess chloro- or dichlorodimethyl ether as the solvent was not advantageous.

TABLE 1

Chloromethylation of 3,5-Dimethylisoxazole

Expt. No.	Chloromethylating agent	Catalyst	Medium	Reaction conditions	Yield (in %)		Comments
					on dimethylisoxazole used	on dimethylisoxazole reacted	
1	Paraformaldehyde – HCl	$ZnCl_2$	Dichloroethane	HCl passed for 1.5 hours at 55-60°, boiled for 3 hours	30	46	35% dimethyl isoxazole recovered. Insignificant tar formation
2	Paraformaldehyde – HCl	$ZnCl_2$	"	HCl passed for 3 hours at 75°, boiled for 5 hours	26	26	No dimethylisoxazole recovered. Strong tar formation
3	Paraformaldehyde – HCl	$ZnCl_2$	Conc. HCl	Heating for 12 hours at 68-72°	23	25	8% dimethylisoxazole recovered. Strong tar formation
4	CH_2ClOCH_2Cl	$ZnCl_2$	Chloroform	Boiling for 12 hours	29	48	40% dimethylisoxazole recovered. Insignificant tar formation
5	CH_2ClOCH_2Cl	$ZnCl_2$	Dichloroethane	Boiling for 14 hours	30	30	No dimethylisoxazole recovered. Strong tar formation
6	CH_2ClOCH_2Cl	$ZnCl_2$	Excess CH_2ClOCH_2Cl	Heating at 50-60° for 14 hours	20	24	15% dimethylisoxazole recovered. Strong tar formation
7	CH_2ClOCH_2Cl	$SnCl_4$	Chloroform	Boiling for 6 hours	12	18.5	35% dimethyl isoxazole recovered. Insignificant tar formation
8	CH_2ClOCH_2Cl	Conc. H_2SO_4	Conc. H_2SO_4	Heating at 70-80° for 4 hours	0	0	45% dimethylisoxazole recovered. Strong tar formation
9	CH_2ClOCH_3	$ZnCl_2$	Excess CH_2ClOCH_3	Heating at 60° for 12 hours	21	33	37% dimethylisoxazole recovered. Considerable tar formation
10	CH_2ClOCH_3	$ZnCl_2$	The same	Boiling for 18 hours	12	18.5	35% dimethylisoxazole recovered. Strong tar formation
11	CH_2ClOCH_3	$ZnCl_2$	"	Boiling for 12 hours	2.5	3.5	20% dimethylisoxazole recovered. Strong tar formation.

Under the established optimal conditions (experiments 1 and 4), the chloromethylation of 3,5-dimethylisoxazole proceeded extremely smoothly and gave steady yields; the reaction product was isolated by the usual methods. We also attempted to establish the composition of the tarry residue, obtained in different amounts during chloromethylation under various conditions. By distillation we were able to isolate a very small amount of a substance with m.p. 72-74°, which differed, however, in analysis from bis-(3,5-dimethylisoxazolyl)-methane, whose formation could be expected; evidently, it was a more complex polycondensation product.

In order to widen the application of this reaction and to study the effect of alkyl substituents on the result of chloromethylation, we then studied the chloromethylation of 3- and 5-methylisoxazoles, isoxazole itself and also 5-phenylisoxazole under the optimal conditions. The experimental results are given in Table 2.

TABLE 2

Chloromethylation of Isoxazole and Its Homologs

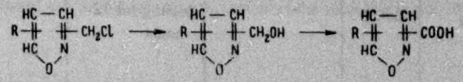
Expt. No.	Starting compound	Solvent	Reaction conditions	Yield (in % of isoxazole taken)
1	3,5-Dimethylisoxazole	Dichloroethane	HCl passed for 2 hours at 52°, boiling for 3 hours	30
2	5-Methylisoxazole	"	HCl passed for 2 hours at 60°, boiling for 3 hours	26
3	3-Methylisoxazole	"	HCl passed for 3 hours at 60°, boiling for 4 hours	19.5
4	Isoxazole	Chloroform	HCl passed for 8 hours at boiling point, boiling for 8 hours	1.8

The results obtained indicate very clearly that the yield of chloromethylation product fell with a decrease in the number of substituent methyl groups in the isoxazole nucleus. With isoxazole itself, the chloromethylation proceeded to the least extent and despite many attempts and variations in the conditions, we were unable to change the result and to isolate the chloromethylation product in an analytically pure state.

Thus, as in the aromatic series, chloromethylation in a heterocyclic ring is facilitated by the presence of a substituent of the first order in the nucleus and, consequently, it obeys the law of electrophilic substitution in the isoxazole series. This further confirms the fact that the isoxazole system represents a typical aromatic system here. At the same time we should note that under the same conditions, the aromatic analogs of the compounds we used (benzene, toluene and xylene) are chloromethylated much more readily, which indicates the relative inertness of the isoxazole ring in electrophilic substitution reactions, which in this connection exceeds not only such "superaromatic" heterocycles as pyrrole, thiophene and furan, but also benzene.

In contrast to 3,5-dimethylisoxazole, chloromethylation of 3- and 5-methylisoxazoles can lead to the formation of one or another isomer or a mixture of both possible isomers. Investigation showed that chloromethylation of both 3-methylisoxazole and 5-methylisoxazole gave only one reaction product; thus, the chloromethylation reaction goes practically in one direction. Thus, the reaction mixture obtained by the chloromethylation of 5-methylisoxazole, was distilled on a vacuum column and 90% of it came over in a range of 0.1-0.2°. The very small amount of light fraction possibly contained some impurities, whose presence should not be explained by the chloromethylation proceeding in more than one direction, but by the presence of traces of isomers in the starting 3- and 5-methylisoxazoles, as the method of preparing them [12, 13] did not exclude the presence of a few percent of other isomers in them.

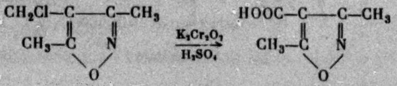
To solve the problem of the structure of the chloromethyl derivatives obtained, we developed a method of converting them into the corresponding isoxazolyl carbinols and then into the isoxazolecarboxylic acids by the scheme



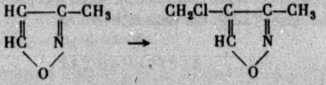
Hydrolysis of chloromethyl derivatives of the isoxazole series into the corresponding alcohols involves difficulties as the isoxazole ring is readily opened by treatment with substances of an alkaline character. One of us and A.Ia. Khorlin attempted to prepare 3-hydroxymethylisoxazole from the corresponding chloride through the acetate [11]. Although the acetate was obtained in high yield, it could not be hydrolyzed.

We have now devised conditions for the direct hydrolysis of chloromethyl derivatives into the corresponding hydroxymethylisoxazoles by heating the chlorides with an aqueous suspension of freshly precipitated lead oxide. By this method, the alcohols were obtained in high yields (60-70%) and the reaction put forward is a new and preparatively-convenient method of obtaining hydroxymethylisoxazoles, which, up to now, could only be obtained through the corresponding difficultly accessible aminomethylisoxazoles [13]. Considering the availability of chloromethylisoxazoles by direct chloromethylation, the method of synthesizing hydroxymethylisoxazoles that we proposed is quite obviously preferable.

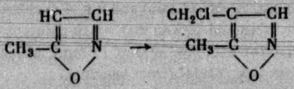
Oxidation of the hydroxymethylisoxazoles obtained to the corresponding acids did not present difficulties and was performed by a known method [13], using chromic mixture. The isoxazolecarboxylic acids were thus obtained in high yields. The isoxazolecarboxylic acids could be obtained by direct oxidation of the chloromethyl derivatives with chromic mixture, by-passing the corresponding carbinols, and this has preparative value; we used this method to prepare 3,5-dimethylisoxazole-4-carboxylic acid and to prove the structure of the chloromethylation product of 5-phenylisoxazole (see below).



When the chloromethylation product of 3-methylisoxazole was hydrolyzed, we obtained a liquid 3-methylhydroxymethylisoxazole, whose p-nitrobenzoate had m.p. 130-132°. This constant differed sharply from the constant of the p-nitrobenzoate of 3-methyl-5-hydroxymethylisoxazole (m.p. 82-83° [13]), whose formation would be expected. Oxidation of the alcohol obtained gave, as the sole reaction product, a 3-methylisoxazolecarboxylic acid with m.p. 121-122°, while 3-methylisoxazole-5-carboxylic acid has m.p. 210-211° [13, 14]. Thus, we were obviously dealing with 3-methylisoxazole-4-carboxylic acid and 3-methyl-4-hydroxymethylisoxazole, which are not described in the literature, and, consequently, the chloromethylation product of 3-methylisoxazole was 3-methyl-4-chloromethylisoxazole.



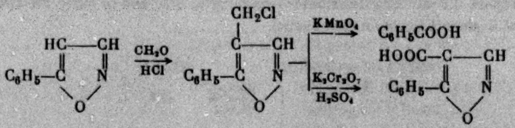
Exactly the same hydrolysis of the chloromethylation product of 5-methylisoxazole gave, as the sole reaction product, a hydroxymethylisoxazole, whose p-nitrobenzoate had m.p. 125-126° and oxidation of the alcohol gave only an acid with m.p. 146-147°. The two substances differed sharply in constants from the p-nitrobenzoate of 5-methyl-3-hydroxymethylisoxazole and 5-methylisoxazole-3-carboxylic acid (m.p. 92-93° [13] and 176-177° [13, 14], respectively). Consequently, the compounds we obtained were 5-methyl-4-hydroxymethylisoxazole and 5-methylisoxazole-4-carboxylic acid, respectively, which are not described in the literature.



To prove the absence of traces of isomeric chloromethyl derivatives in the chloromethylation reaction product, we investigated the small, most volatile fraction, obtained on distilling the chloromethylation product of 5-methylisoxazole on a column (see above). Without any purification, the latter was treated with the silver salt of p-nitrobenzoic acid. The p-nitrobenzoate of isomeric 5-methyl-3-hydroxymethylisoxazole could not be isolated from the mixture of p-nitrobenzoates of isoxazolylcarbinols thus obtained.

The insufficiency of the amount of chloromethylation product from isoxazole itself and the difficulties arising in its purification, prevented us from determining the structure of this substance similarly; however, there can be hardly any doubt that it was 4-chloromethylisoxazole. We have now proved definitely that nitration of isoxazole occurs at position 4, confirming this proposal. Data on the nitration will be published in the next communication.

On chloromethylating 5-phenylisoxazole with paraformaldehyde and hydrogen chloride in dichloroethane in the presence of zinc chloride, we obtained a solid chloromethyl derivative in 37% yield. Oxidation of the latter with potassium permanganate gave a high yield of benzoic acid; phthalic acids were not detected in the oxidation products. Hence it follows that chloromethylation of 5-phenylisoxazole proceeded exclusively in the isoxazole ring and did not involve the phenyl group in the least. To determine the position in which the chloromethyl group was introduced, we attempted to carry out the conversions in the scheme described previously for the methylisoxazoles. However, hydrolysis of 5-phenylchloromethylisoxazole gave an oily mixture of products. As a result, we used the direct oxidation of the chloromethyl derivative with chromic mixture, which gave about 70% yield of an acid with m.p. 148-149°, which was close in its properties to 5-phenylisoxazole-4-carboxylic acid, which is described in the literature. The conversions described can be represented by the following scheme.



From the material presented it is obvious that chloromethylation of 5-phenylisoxazole proceeded in position 4 of the isoxazole nucleus. This confirms data from one of our previous reports [15] that electrophilic substitution in 5-phenylisoxazole occurs at position 4. Thus, in the 5-phenylisoxazole system the isoxazole nucleus is more active than the phenyl, with the latter very clearly showing an activating effect. Thus, for example, isoxazole itself is only chloromethylated to a low degree (yield, 1.8%), but with phenylisoxazole the yield is 37%. Moreover, the phenyl nucleus activates the isoxazole ring more strongly than methyl groups, as is shown by the yields of chloromethyl derivatives (37, 26 and 19%, respectively), obtained under the same conditions.

From the data presented, it is obvious that chloromethylation of substituted isoxazoles proceeds only in position 4 (regardless of the position of other substituents), when this position in the nucleus is free, and consequently, position 4 is the most active one in the isoxazole nucleus.

EXPERIMENTAL

4-Chloromethyl-3,5-dimethylisoxazole. a) For 1.5-2 hours a fast stream of hydrogen chloride was passed into a vigorously stirred mixture of 20 g of dimethylisoxazole, 8 g of paraformaldehyde, 10 g of anhydrous zinc chloride and 50 ml of dichloroethane at 50-55°. The mixture was then boiled for three hours and poured into water, the dichloroethane layer separated, the aqueous layer carefully neutralized with potash, extracted with chloroform and then saturated with potash, the zinc hydroxide removed by filtration and the aqueous layer again extracted with chloroform. The combined extracts were washed with sodium bicarbonate solution and water and dried over calcium chloride. The solvent was evaporated and the residue vacuum distilled to give 11 g of the original 3,5-dimethylisoxazole with b.p. 30-40° (7 mm) and 9 g of 4-chloromethyl-3,5-dimethylisoxazole (30% calculated on the dimethylisoxazole taken and 46% on that which reacted) with b.p. 88-90% (7 mm). Distillation of the tarry residue yielded a fraction with b.p. 90-150° (7 mm), which, on standing, deposited a small amount of a crystalline substance with m.p. 73-74° (from benzine).

b) Heating a mixture of 25 g of 3,5-dimethylisoxazole and 15 g of paraformaldehyde in 130 ml of concentrated hydrochloric acid at 68-72° for 12 hours, treating the mixture with sodium hydroxide solution, extracting with benzene and working up in the usual way yielded 8.5 g of 4-chloromethyl-3,5-dimethylisoxazole (23%) and 2 g of starting dimethylisoxazole.

c) A mixture of 15 g of 3,5-dimethylisoxazole, 25 g of dichlorodimethyl ether, 8 g of anhydrous zinc chloride, 1 ml of water and 40 ml of chloroform was boiled for 12 hours with vigorous stirring. The mixture was poured into water, the chloroform layer separated and the aqueous layer neutralized with bicarbonate solution and extracted with chloroform. The combined extracts were treated as described above and yielded 6.5 g of 4-chloromethyl-3,5-dimethylisoxazole (29 and 48%, respectively, on the dimethylisoxazole taken and consumed) with b.p. 88-90° (7 mm) and 6 g of starting dimethylisoxazole.

The chloromethylation with monochloromethyl ether was performed under analogous conditions. The conditions of the other chloromethylation experiments, which are not of preparative interest, are shown by the data in Table 1. After redistillation, the 4-chloromethyl-3,5-dimethylisoxazole had the constants:

B.p. 67-67.5° (1 mm), n_D^{20} 1.4852, d_4^{20} 1.1738, MR_D 5.55; calc. 35.49.*

Found %: Cl 24.63, 24.66. C_6H_8ONCl. Calculated %: Cl 24.36.

The colorless oil was lachryma[illegible], difficultly soluble in water and stable during storage.

3-Methyl-4-chloromethylisoxazole. This was prepared by the method a described above from 34 g of 3-methylisoxazole [11], 18 g of paraformaldehyde and 21 g of zinc chloride in 100 ml of dichloroethane. The hydrogen chloride was passed for three hours at 60-65° and the mixture boiled for three hours. Distillation yielded 13 g (37%) of original 3-methylisoxazole with b.p. 35-50° (50 mm) and 10 g (19.5%) of the chloromethylation product with b.p. 71-81° (9 mm).

B.p. 61-62° (1 mm), n_D^{20} 1.4874, d_4^{20} 1.2026, MR_D 31.49; calc. 31.00.

Found %: Cl 26.71, 26.84. C_5H_6ONCl. Calculated %: Cl 26.99.

3-Methyl-4-chloromethylisoxazole was a colorless mobile liquid, soluble in ether, chloroform and alcohol and lachrymatory.

5-Methyl-4-chloromethylisoxazole. This was prepared by method a from 37 g of 5-methylisoxazole [12], 20 g of paraformaldehyde, 24 g of zinc chloride in 100 ml of dichloroethane. The hydrogen chloride was passed for 3.5 hours at 60-70° and the reaction mixture boiled for four hours. Distillation yielded 9 g (24%) of original 5-methylisoxazole with b.p. 35-40° (40 mm) and 17 g (29% on the 5-methylisoxazole taken and 39% on that reacted) of chloromethylation product with b.p. 78-80° (9 mm). Distillation on a vacuum column of 12 theoretical plates yielded 0.8 g of a fraction with b.p. 74-78° (6 mm) and 12 g of the main fraction.

B.p. 78° (6 mm), n_D^{20} 1.4883, d_4^{20} 1.2028, MR_D 31.54; calc. 31.00.

Found %: Cl 26.74, 26.76. C_5H_6ONCl. Calculated %: Cl 26.99.

5-Methyl-4-chloromethylisoxazole was a colorless, mobile, lachrymatory liquid; it dissolved in ether, chloroform and alcohol. It darkened on prolonged storage.

4-Chloromethylisoxazole was obtained from 27 g of isoxazole [16], 17 g of paraformaldehyde, 20 g of zinc chloride in 120 ml of chloroform by method a. The hydrogen chloride was passed for eight hours with the reaction mixture boiling, then the latter was boiled for eight hours. The solvent was removed using an efficient fractionating column; the residue was vacuum distilled twice. The yield was 0.8 g (1.8%). The b.p. was 63-64° (5 mm), n_D^{20} 1.4742, d_4^{20} 1.2337. 4-Chloromethylisoxazole was a colorless, mobile liquid, which readily dissolved in ether, alcohol, chloroform and benzene; it was weakly lachrymatory and yellowed on standing.

5-Phenyl-4-chloromethylisoxazole was prepared by method a from 28 g of 5-phenylisoxazole [17], 9 g of paraformaldehyde and 10 g of zinc chloride in 150 ml of dichloroethane. The hydrogen chloride was passed for 2.5 hours at 60-65° and then the reaction mixture boiled for 3.5 hours. The solvent was removed and the residue heated on a boiling water bath at 15 mm for one hour and then left for 10-12 hours at 10-15°. The colorless crystals formed were filtered off. The mother liquors consisted of 5-phenylisoxazole and a small amount of chloromethyl derivative dissolved in it, which could be partially isolated by freezing out. We isolated 16 g (57%) of the original 5-phenylisoxazole and 11.5 g (37% calculated on the phenylisoxazole used in the reaction) of product with m.p. 51-52° (from alcohol).

Found %: Cl 18.63, 18.42. $C_{10}H_8ONCl$. Calculated %: Cl 18.30.

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*In calculating the MR_D, the ring-nitrogen increment was taken as 2.84, as in all work in this series.

5-Phenyl-4-chloromethylisoxazole was a colorless, crystalline substance, which was readily soluble in ether and benzene, more difficultly so in alcohol and insoluble in water.

3,5-Dimethyl-4-hydroxymethylisoxazole. A mixture of 14.5 g of 3,5 dimethyl-4-chloromethylisoxazole and 38 g of freshly precipitated lead oxide in 100 ml of water was boiled with stirring for three hours. The precipitate was filtered off, the filtrate extracted with ether in an extractor and the ether extracts dried over sodium sulfate and evaporated in vacuum without heating. The crystals formed were filtered off and recrystallized from ether, when they had m.p. 73-74°. The yield was 8.5 g (67%).

Found %: C 56.80, 56.94; H 7.45, 7.39. $C_6H_9O_2N$. Calculated %: C 56.68; H 7.13.

3,5-Dimethyl-4-hydroxymethylisoxazole formed colorless crystals, which were readily soluble in water and alcohol.

5-Methyl-4-hydroxymethylisoxazole was prepared similarly to the above from 12 g of 5-methyl-4-chloromethylisoxazole (isolated after distillation on a column) and 26 g of freshly precipitated lead oxide. After evaporation of the ether, the residue was vacuum distilled twice. The yield was 6.3 g (60%).

B.p. 109° (3 mm), n_D^{20} 1.4835, d_4^{20} 1.1958, MR_D 27.04; calc. 27.53.

Found %: C 53.41, 53.64; H 6.52, 6.52. $C_5H_7O_2N$. Calculated %: C 53.09; H 6.24.

5-Methyl-4-hydroxymethylisoxazole was a colorless, viscous liquid with a mintlike smell. It was readily soluble in water, alcohol and ether.

The p-nitrobenzoate was prepared from 0.55 g of 5-methyl-4-hydroxymethylisoxazole and 1.0 g of p-nitrobenzoyl chloride, dissolved in pyridine, which was heated on a boiling water bath for 20 minutes; the cooled reaction mixture was poured into water. The crystals formed were filtered off and washed with sodium hydroxide solution. After recrystallization from benzine (90-100°), the substance had m.p. 125-126°.

Found %: C 55.21, 55.18; H 3.90, 3.95. $C_{12}H_{10}O_5N_2$. Calculated %: C 54.96; H 3.81.

3-Methyl-4-hydroxymethylisoxazole. This was prepared as described above from 8.5 g of 3-methyl-4-chloromethylisoxazole and 18 g of freshly precipitated lead oxide. After two distillations, we obtained 5.1 g (70%) of material.

B.p. 100-101° (1 mm), n_D^{20} 1.4839, d_4^{20} 1.1956, MR_D 27.09; calc. 27.53.

Found %: C 52.81, 52.94; H 6.35, 6.40. $C_5H_7O_2N$. Calculated %: C 53.09; H 6.24.

3-Methyl-4-hydroxymethylisoxazole was a viscous, colorless liquid with a spicy smell and was readily soluble in water, alcohol and ether. The p-nitrobenzoate was obtained similarly to the p-nitrobenzoate of 5-methyl-4-hydroxymethylisoxazole, described above. The m.p. was 130-132° (from benzine).

Found %: C 54.90, 54.78; H 3.70, 3.75. $C_{12}H_{10}O_5N_2$. Calculated %: C 54.96; H 3.81.

3,5-Dimethylisoxazole-4-carboxylic acid. A. 20 ml of concentrated sulfuric acid was added dropwise to a mixture of 3.5 g of 3,5-dimethyl-4-hydroxymethylisoxazole and 10 g of potassium bichromate in 30 ml of water. The mixture was heated for one hour on a boiling water bath, 5 g of ammonium sulfate added and the whole shaken. The colorless crystals which precipitated were filtered off and washed with dilute hydrochloric acid. The yield was 3 g. The filtrate was extracted with ether and the ether evaporated without heating. We obtained an extra 0.2 g of substance. The total yield was 3.2 g (82%). After recrystallization from water and benzene, the material had m.p. 141-142°.

Found %: C 51.38, 51.24; H 5.17, 5.10. $C_6H_7O_3N$. Calculated %: C 51.06; H 5.00.

3,5-Dimethylisoxazole-4-carboxylic acid was a colorless, crystalline substance, which was readily soluble in ether and alcohol.

B. 50 ml of concentrated sulfuric acid was added dropwise to a mixture of 7 g of 3,5-dimethyl-4-chloromethylisoxazole and 30 g of potassium bichromate in 100 ml of water, the mixture heated up and boiled. When the boiling ceased, 15 g of ammonium sulfate was added. The crystals, which precipitated after cooling, were filtered off and washed with 10% hydrochloric acid. The yield was 5 g (73%). After recrystallization from water, the substance had m.p. 141-142°. A mixed melting point with the sample prepared by method A was not depressed.

5-Methylisoxazole-4-carboxylic acid. This was prepared by method A, described for 3,5-dimethylisoxazole-4-carboxylic acid, from 1.6 g of 5-methyl-4-hydroxymethylisoxazole, 5 g of potassium bichromate in 20 ml of water and 12 ml of sulfuric acid. The yield was 1.7 g (94%). After recrystallization from water, the substance had m.p. 146-147°.

Found %: C 47.00, 46.74; H 4.07, 3.99. $C_5H_5O_3N$. Calculated %: C 47.24; H 3.88.

5-Methylisoxazole-4-carboxylic acid formed colorless crystals, which were readily soluble in ether and chloroform.

3-Methylisoxazole-4-carboxylic acid. This was prepared similarly by method A from 2 g of 3-methyl-4-hydroxymethylisoxazole, 7 g of potassium bichromate in 25 ml of water and 15 ml of sulfuric acid. The yield was 2.2 g (99%). After recrystallization from water and benzene, the substance had m.p. 121-122°.

Found %: C 47.44, 47.25; H 4.12, 4.00. $C_5H_5O_3N$. Calculated %: C 47.24; H 3.88.

3-Methylisoxazole-4-carboxylic acid was a colorless, crystalline substance, which was soluble in alcohol and ether.

5-Phenylisoxazole-4-carboxylic acid. This was prepared by method B, described for 3,5-dimethylisoxazole-4-carboxylic acid, from 0.75 g of 5-phenyl-4-chloromethylisoxazole, 1.7 g of potassium bichromate in 15 ml of water and 5 ml of sulfuric acid. The substance was recrystallized from water and benzene. The m.p. was 148 to 149°. The yield was 0.5 g (68%).

Found %: C 63.26; H 3.85. $C_{10}H_7O_3N$. Calculated %: C 63.49; H 3.73.

5-Phenylisoxazole-4-carboxylic acid was a colorless, crystalline substance, which was readily soluble in alcohol and ether. According to literature data [18], the m.p. is 155-156°.

The filtrate and mother liquors from recrystallization did not contain other isomeric phenylisoxazolecarboxylic acids.

Oxidation of 5-phenyl-4-chloromethylisoxazole with potassium permanganate. A mixture of 1.0 g of 5-phenyl-4-chloromethylisoxazole and 6.5 g of potassium permanganate in 50 ml of water was boiled for six hours. The manganese dioxide formed was filtered off and the filtrate cooled, evaporated to small volume and acidified with hydrochloric acid. The acid liberated was filtered off to give colorless crystals with m.p. 121-121.5° (from water). The yield was 0.4 g (65%). A mixed melting point with an authentic sample of benzoic acid was not depressed. Other reaction products could not be detected in the mother liquors from the recrystallization. Oxidation of the mother liquor, left after separation of the 5-phenyl-4-chloromethylisoxazole from the chloromethylation reaction (see above), was performed similarly and yielded benzoic acid (yield 80%) with m.p. 121-122°.

SUMMARY

1. A method of synthesizing chloromethylisoxazoles by chloromethylating the corresponding isoxazoles was developed. It was shown that the best results were obtained by chloromethylation with paraformaldehyde and hydrogen chloride in the presence of zinc chloride in dichloroethane and chloromethylation with dichlorodimethyl ether.

2. It was shown that the ease of chloromethylation in the isoxazole series increased with an increase in the number of methyl groups in the nucleus.

3. It was shown that in all cases when position 4 in the isoxazole nucleus was not substituted, the chloromethylation reaction occurred at this position. This was also true for 5-phenylisoxazole.

4. A method was developed for hydrolyzing chloromethylisoxazoles into the corresponding alcohols by heating the chlorides with an aqueous suspension of lead oxide.

5. A method was developed for direct oxidation of substituted chloromethylisoxazoles into the corresponding isoxazolecarboxylic acids.

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*Original Russian pagination. See C.B. translation.

HETEROCYCLIC COMPOUNDS

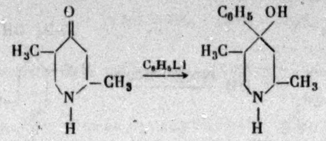
63. SYNTHETIC ANALGESICS. XXVI. STEREOISOMERISM OF 2,5-DIMETHYL-4-PIPERIDOLS AND 1-ACYL-2,5-DIMETHYL-4-PHENYL-4-PIPERIDOLS

I.N. Nazarov,* N.S. Prostakov and N.N. Mikheeva

Continuing our investigations in the series of 1-alkyl-2,5-dimethyl-4-aryl-4-piperidols and their esters, in which class promedol, isopromedol and α-promedol belong [1], we synthesized the analogs of these piperidine alcohols in which an acyl radical was substituted on the nitrogen.

We also synthesized the stereoisomeric 2,5-dimethyl-4-phenyl-4-piperidols and were able to convert them to the earlier described stereoisomeric 1,2,5-trimethyl-4-phenyl-piperidols [1].

We obtained 2,5-dimethyl-4-phenyl-4-piperidol (II) in 40% yield by reacting phenyllithium with 2,5-dimethyl-4-piperidone (I).



(I) (II)

Of the four theoretically possible stereoisomers of 2,5-dimethyl-4-phenyl-4-piperidol (II) we isolated the γ-isomer and the α-isomer in crystalline form. The third isomer of piperidol (II), formed in the indicated reaction, was isolated as the N-acetyl derivative, described below.

We used chromatography on aluminum oxide and recrystallization to separate the mixed stereoisomeric 2,5-dimethyl-4-phenyl-4-piperidole.

The low-melting γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (II) constituted approximately 85-90% of the total mixture of crystalline isomers. When methylated with either formaldehyde or methyl iodide it was converted to the γ-isomer of 1,2,5-trimethyl-4-phenyl-4-piperidol (III), which is also obtained as the main product when phenyllithium is reacted with 1,2,5-trimethyl-4-piperidone [1].

The methylation of the α-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (II) gave the α-isomer of piperidol (III).

In the present paper we also used chromatography to separate the mixed stereoisomeric 1,2,5-trimethyl-4-phenyl-4-piperidole (III). Here it was found that aluminum oxide displays a different adsorption capacity toward the stereoisomeric piperidols (II) and (III). For both 1,2,5-trimethyl-4-phenyl-4-piperidol and 2,5-dimethyl-4-phenyl-4-piperidol the stereoisomeric alcohols, adsorbed by aluminum oxide, are eluted by chloroform in the following order: γ,β-, and then the α-isomer (the β-isomer was isolated in the case of separating the mixed stereoisomeric 1,2,5-trimethyl-4-phenyl-4-piperidols).

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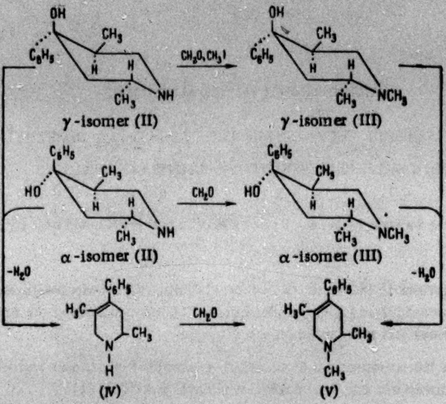
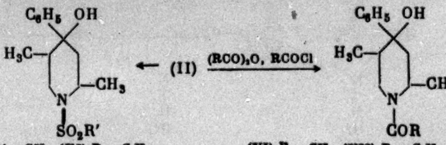
*Deceased.

The γ- and α-isomers of 2,5-dimethyl-4-phenyl-4-piperidol (II) when dehydrated with 70% sulfuric acid give the same product, namely 2,5-dimethyl-4-phenyl-1,2,3,6-tetrahydropyridine (IV), which on methylation is converted to 1,2,5-trimethyl-4-phenyl-1,2,3,6-tetrahydropyridine (V). The latter is also formed when either the γ- or the α-isomer of 1,2,5-trimethyl-4-phenyl-4-piperidol (III) is dehydrated.


OH
CH3
C6H5
H
H
CH3
NH
γ-isomer (II)
CH2O, CH3I
OH
CH3
C6H5
H
H
CH3
NCH3
γ-isomer (III)
C6H5
CH3
HO
H
H
CH3
NH
α-isomer (II)
CH2O
C6H5
CH3
HO
H
H
CH3
NCH3
α-isomer (III)
-H2O
-H2O
C6H5
H3C
CH3
N
H
(IV)
CH2O
C6H5
H3C
CH3
N
CH3
(V)

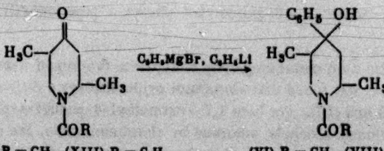
The acylation of the 2,5-dimethyl-4-phenyl-4-piperidols (II) with either acid anhydrides or acid chlorides readily gave the corresponding N-acyl derivatives:


C6H5 OH
H3C
CH3
N
SO2R′
(II)
(RCO)2O, RCOCl
C6H5 OH
H3C
CH3
N
COR

(X) R′ = CH_3, (XI) R = C_6H_5 (VI) R = CH_3, (VII) R = C_2H_5, (VIII) R = C_6H_5, (IX) R = $CH_2N(C_2H_5)_2$

In this manner we obtained the following in yields up to 85%: (VI) 1-acetyl-, (VII) 1-propionyl-, (VIII) 1-benzoyl-, (IX) 1-diethylaminoacetyl-, (X) 1-methylsulfonyl- and (XI) 1-benzenesulfonyl-2,5-dimethyl-4-phenyl-4-piperidol.

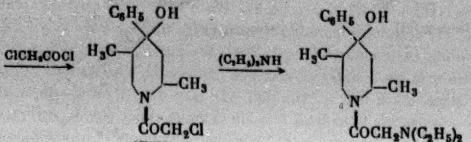
The acetylation of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (II) gave the γ-isomer of 1-acetyl-2,5-dimethyl-4-phenyl-4-piperidol (VI), while from the α-isomer of piperidol (II) we obtained the α-isomer of piperidol (VI). Besides these two stereoisomeric piperidols (VI), we also obtained a third isomer of 1-acetyl-2,5-dimethyl-4-phenyl-4-piperidol when we reacted 1-acetyl-2,5-dimethyl-4-phenyl-4-piperidone (XII) with either phenylmagnesium bromide or phenyllithium.


O
H3C
CH3
N
COR
C6H5MgBr, C6H5Li
C6H5 OH
H3C
CH3
N
COR

(XII) R = CH_3, (XIII) R = C_6H_5 (VI) R = CH_3, (VIII) R = C_6H_5

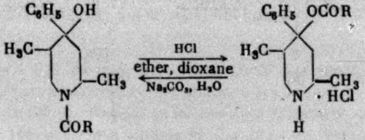
The same isomer of piperidol (VI) was also isolated when the noncrystalline residue, obtained after removal of the α- and γ-isomers of 2,5-dimethyl-4-phenyl-4-piperidol (II) in the reaction of 2,5-dimethyl-4-piperidone

(I) with phenyllithium, was acetylated. The γ-isomer of 1-diethylaminoacetyl-2,5-dimethyl-4-phenyl-4-piperidol (IX) was obtained by the acylation of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol with chloroacetyl chloride, followed by reaction of the 1-chloroacetyl-2,5-dimethyl-4-piperidol (XIV) formed with diethylamine.



(XIV) (IX)

The γ-isomers of 1-acetyl- and 1-propionyl-2,5-dimethyl-4-phenyl-4-piperidol when treated with dry hydrogen chloride in either dioxane or ether solution are, respectively, converted to the hydrochlorides of the acetic (XV) and propionic (XVI) esters of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol. The latter in weakly alkaline media are reconverted to the original piperidols (VI) and (VII) [2].



(XV) $R = CH_3$, (XVI) $R = C_2H_5$

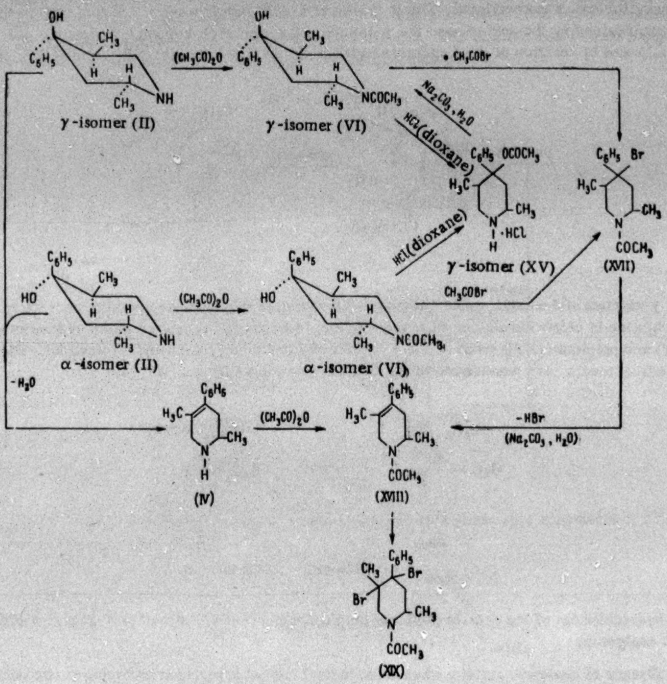
The hydrochlorides of the acetate (XV) and propionate (XVI) of 2,5-dimethyl-4-phenyl-4-piperidol are inactive as analgesics.

The absence of analgesic activity when an N-methyl radical is replaced by hydrogen also occurs in other series of synthetic analgesics [3]. The α-isomer of 1-acetyl-2,5-dimethyl-4-phenyl-4-piperidol (VI) under the same conditions (treatment with hydrogen chloride in dioxane) is not converted to the hydrochloride of the acetate of the α-isomer of 2,5-dimethyl-4-phenyl-4-piperidol, but instead gives the same hydrochloride of the acetate of the γ-isomer (XV) described above, which when treated with aqueous soda solution is converted to the γ-isomer of 1-acetyl-2,5-dimethyl-4-phenyl-4-piperidol (VI).

A similar change in the configuration of the α-isomer to that of the corresponding γ-isomer was also observed by us in the replacement of the hydroxyl group in piperidols (VI) by bromine. Both of the stereoisomeric alcohols (VI) when reacted with acetyl bromide [4] give the same γ-isomer of 1-acetyl-2,5-dimethyl-4-phenyl-4-bromopiperidine (XVII).

The bromo derivative (XVII) is easily debrominated to give 1-acetyl-2,5-dimethyl-4-phenyl-1,2,3,6-tetrahydropyridine (XVIII). The latter was also obtained by the acetylation of 2,5-dimethyl-4-phenyl-1,2,3,6-tetrahydropyridine (IV), described above. The bromination of 1-acetyl-2,5-dimethyl-4-phenyl-1,2,3,6-tetrahydropyridine gave 1-acetyl-2,5-dimethyl-4-phenyl-4,5-dibromopiperidine (XIX) in 87% yield.

The obtained results make it possible to postulate that the γ- and α-isomers of piperidole (II), (III) and (VI) belong to the same series of trans-piperidones (starting products in their synthesis) and differ among themselves in the position of the phenyl radical and hydroxyl group on the fourth carbon atom; here the more stable γ-form corresponds to a trans-position of the methyl groups and a trans-position of the phenyl radical with respect to the methyl group found on carbon 5 of the piperidine ring. In like manner the α-form corresponds to a trans-position of the methyl groups and a cis-position of the phenyl radical with respect to the same methyl group.


γ-isomer (II)
(CH₃CO)₂O
γ-isomer (VI)
+ CH₃COBr
Na₂CO₃, H₂O
HCl(dioxane)
γ-isomer (XV)
(XVII)
α-isomer (II)
(CH₃CO)₂O
α-isomer (VI)
HCl(dioxane)
CH₃COBr
-H₂O
(IV)
(CH₃CO)₂O
(XVIII)
-HBr
(Na₂CO₃, H₂O)
(XIX)

EXPERIMENTAL

2,5-Dimethyl-4-phenyl-4-piperidol (II). a) Phenyllithium was obtained from 57 g of lithium and 650 g of bromobenzene in 1000 ml of absolute ether. Then 150 g of 2,5-dimethyl-4-piperidone (I) was added dropwise in three hours. The reaction mixture was stirred for another hour at room temperature, and then it was decomposed with water and hydrochloric acid (first with 200 ml of water, then with 200 ml of 18% hydrochloric acid, and finally with 300 ml of concentrated hydrochloric acid). The water layer was treated with potassium hydroxide (excess). The organic bases that separated were extracted with ether, then dried over sodium sulfate, and finally vacuum-distilled. The following fractions were collected: 1st, 74-199° (3 mm), 29 g; 2nd, 110-160° (3 mm), 93.8 g; 3rd, 160-180° (3 mm), 35.3 g; residue 46 g.

We obtained 25 g of starting 2,5-dimethyl-4-piperidone (I) from the first fraction. The second and third fractions were dissolved in gasoline. The solutions on cooling to room temperature deposited crystals. After the first crops of crystals were removed the mother liquors were evaporated to give a second crop of crystals, which were recrystallized from gasoline. We obtained 38 g of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (II) with m.p. 121-122°.

Found % N 6.59, 6.61. $C_{13}H_{19}ON$. Calculated % N 6.84.

In addition, we also isolated another 4.6 g of the α-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (II) with m.p. 163-166°.

Found % N 7.18, 7.03. $C_{13}H_{19}ON$. Calculated % N 6.84.

A noncrystallizing oil remained after removal of the crystalline piperidols (II).

b) A mixture of the stereoisomers of 2,5-dimethyl-4-phenyl-4-piperidol (II) was obtained as described above. For the reaction we took 19 g of lithium, 225 g of bromobenzene, 50 g of 2,5-dimethyl-4-piperidone and 500 ml of absolute ether. Fractional distillation of the principal reaction products in vacuo gave 6 g of unreacted 2,5-dimethyl-4-piperidone (I) (b.p. 40-93° at 4 mm), 36.9 g of mixed piperidole (II) (b.p. 138-185° at 3 mm), and 6.3 g of residue. Recrystallization of the mixed piperidols (II) from gasoline gave 15.2 g of crystals with m.p. 104-111°, and 21.7 g of noncrystallizing residue. A chloroform solution of 3 g of the crystals with m.p. 104-111° was passed through a column containing aluminum oxide (the column height was 90 cm and the diameter was 1.5 cm). For elution we first used chloroform, and then methanol. We obtained 2.3 g of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (II) with m.p. 121-122° and 0.4 g of the α-isomer with m.p. 164-166°. The γ-isomer is eluted with chloroform and is found in the first portions of the solvent, while the α-isomer is eluted with methanol toward the end of chromatographing.

Separation of mixed stereoisomeric 1,2,5-trimethyl-4-phenyl-4-piperidole (III) using chromatographing on aluminum oxide. The mixture of stereoisomeric 1,2,5-trimethyl-4-phenyl-4-piperidols (III) was obtained by the procedure described in previous communications [1]. For the reaction we took 50 g of lithium, 565 g of bromobenzene, 423 g of 1,2,5-trimethyl-4-piperidone and 800 ml of ether. Fractional distillation of the principal reaction products in vacuo gave 43 g of starting 1,2,5-trimethyl-4-piperidone (b.p. 54-56° at 3.5 mm), 470 g of mixed piperidols (III) (b.p. 136-138° at 2.5 mm), and 70 g of residue.

Recrystallization of the mixed piperidols (III) from gasoline gave 210 g of the γ-isomer of 1,2,5-trimethyl-4-phenyl-4-piperidol with m.p. 107-108°, 173 g of crystals with m.p. 68-76°, and 85 g of a noncrystallizing residue.

a) A chloroform solution of 4 g of the crystals with m.p. 68-76° was passed through a column containing aluminum oxide (height of lower part of column 80 cm, diameter 1.5 cm, height of upper part of column 10 cm, diameter 2.5 cm, aluminum oxide 160 g). For elution we first used chloroform, and then methanol. We obtained 2.2 g of the γ-isomer with m.p. 105-107° (after washing with gasoline and drying in a desiccator), and 1.3 g of the α-isomer of 1,2,5-trimethyl-4-phenyl-4-piperidol (III) with m.p. 103-105° (recrystallization from gasoline). The γ-isomer is eluted with chloroform and is found in the first portions of solvent, while the α-isomer is eluted with methanol toward the end of chromatographing.

b) A chloroform solution of 20 g of the noncrystalline mixture of piperidols (III) was passed through a column filled with aluminum oxide (height of the lower part of the column 100 cm, diameter 1.5 cm, height of the upper part of the column 40 cm, diameter 2.5 cm, aluminum oxide 280 g). The elution was run as described above, first with chloroform, and then with methanol.

The following fractions were obtained in the order: 0.9 g of the γ-isomer with m.p. 105-107.5°, 4.4 g of the β-isomer with m.p. 96-102°, 0.6 g of crystals with m.p. 118-120°, and 8.6 g of the α-isomer of 1,2,5-trimethyl-4-phenyl-4-piperidol with m.p. 105-107°. The α-isomer was eluted toward the end of chromatographing with methanol. The melting points (and also the weights) were determined after each eluted fraction had been recrystallized from gasoline.

Methylation of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol. a) A mixture of 0.5 g of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (II) (m.p. 121-122°) and 0.6 g of formalin was heated in a sealed ampoule at 130-140° for four hours. The reaction mass was dissolved in 10 ml of water and then treated with potassium hydroxide. The organic bases that separated here were extracted with ether. After drying over sodium sulfate and removal of the ether by distillation we obtained 0.6 g of residue, which crystallized when gasoline was added. We obtained 0.5 g of the γ-isomer of 1,2,5-trimethyl-4-phenyl-4-piperidol (III) with m.p. 107-108°, which did not depress the melting point when mixed with an authentic specimen of this alcohol.

b) A solution of 1 g of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (II) in 30 ml of anhydrous benzene was treated with 3.5 g of methyl iodide. Here an oil deposited on the bottom of the flask. The mixture was heated for five hours at benzene boil. The benzene was decanted, while the residue was dried in a desiccator (1.8 g). Recrystallization of the residue from alcohol gave 0.5 g of the methiodide of the γ-isomer of 1,2,5-trimethyl-4-phenyl-4-piperidol with m.p. 217-221°, which did not depress the melting point when mixed with the methiodide, obtained directly from the γ-isomer of 1,2,5-trimethyl-4-phenyl-4-piperidol (III) and methyl iodide.

Methylation of the α-isomer of 2,5-dimethyl-4-phenyl-4-piperidol. For reaction we took 0.5 g of the α-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (II) (m.p. 163-166°) and 0.6 g of formalin. The reaction was run as described above. We obtained 0.4 g (after two recrystallizations from gasoline) of the α-isomer of 1,2,5-trimethyl-4-phenyl-4-piperidol (III) with m.p. 106-107°. The mixed melting point with the authentic specimen was not depressed.

2,5-Dimethyl-4-phenyl-1,2,3,6-tetrahydropyridine (IV). a) A mixture of 1.5 g of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (II) with m.p. 121-122°, 4 g of 70% sulfuric acid and 0.3 g of fused copper sulfate was heated on the boiling water bath for 4.5 hours. The mixture was diluted with 20 ml of water and then cautiously treated with soda until completely saturated. The free base was extracted with ether, and after drying over sodium sulfate, was vacuum-distilled. We obtained 1.1 g of 2,5-dimethyl-4-phenyl-1,2,3,6-tetrahydropyridine (IV) with b.p. 93° (2.5 mm).

The picrate had m.p. 138-141° (from alcohol).

Found % N 13.78, 13.35. $C_{19}H_{20}O_7N_4$. Calculated % N 13.46.

The hydrochloride of 2,5-dimethyl-4-phenyl-1,2,3,6-tetrahydropyridine had m.p. 143-145° (from acetone).

Found % N 6.59, 6.56. $C_{13}H_{18}NCl$. Calculated % N 6.26.

b) A mixture of 0.5 g of the α-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (II) (m.p. 163-166°), 1.5 g of 70% sulfuric acid and 0.1 g of fused copper sulfate was heated at 90-95° for five hours. The mixture was diluted with water and then carefully treated with soda until saturated. The free base was extracted with ether and then dried over sodium sulfate. Removal of the ether by distillation left 0.3 g of a mobile liquid, from which a picrate with m.p. 141-143° (from alcohol) and a hydrochloride with m.p. 144-145° (from acetone) were obtained. The respective mixtures of the obtained picrate and hydrochloride with the picrate and hydrochloride of 2,5-dimethyl-4-phenyl-1,2,3,6-tetrahydropyridine, obtained from the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol, failed to show a melting point depression.

1,2,5-Trimethyl-4-phenyl-1,2,3,6-tetrahydropyridine (V). a) A mixture of 2 g of the α-isomer of 1,2,5-trimethyl-4-phenyl-4-piperidol (III) (m.p. 106-107°), 4 g of 70% sulfuric acid and 0.5 g of fused copper sulfate was heated at 90-95° for five hours. The mixture was diluted with 20 ml of water and then carefully treated with soda until completely saturated. The free base was extracted with ether, and after drying over sodium sulfate, was vacuum-distilled. We obtained 1.3 g of 1,2,5-trimethyl-4-phenyl-1,2,3,6-tetrahydropyridine (V) with b.p. 85° (2.5 mm), n_D^{17} 1.5479. The picrate had m.p. 126-128° (from alcohol), and failed to depress the melting point when mixed with the picrate of the dehydration product obtained from the γ-isomer of 1,2,5-trimethyl-4-phenyl-4-piperidol [5].

b) A mixture of 3 g of the γ-isomer of 1,2,5-trimethyl-4-phenyl-4-piperidol (III) (m.p. 107-108°) and 10 ml of concentrated hydrochloric acid was heated at 90-95° for three hours. The acid was removed by vacuum-distillation. The glassy residue was dissolved in water. To obtain the free base the water solution was treated with soda, but the addition of the soda gave a floating oil layer, which proved to be insoluble in both saturated aqueous soda solution and in ether. Only after vigorous stirring for a long time with a large excess of soda did the oil layer disappear and the product become soluble in ether. From the latter we isolated 1.8 g of 1,2,5-trimethyl-4-phenyl-1,2,3,6-tetrahydropyridine (V) with b.p. 92-94° (3 mm). It was converted to the picrate, which, the same as the authentic specimen [5], had m.p. 126-128°.

c) A mixture of 1.5 g of 2,5-dimethyl-4-phenyl-1,2,3,6-tetrahydropyridine (IV) and 1.8 g of formalin was heated in a sealed ampoule for four hours at 130-140°. The mixture was diluted with 20 ml of water and then carefully treated with potassium hydroxide until completely saturated. The free base was extracted with ether, and after drying over sodium sulfate, was vacuum-distilled. We obtained 0.9 g of 1,2,5-trimethyl-4-phenyl-1,2,3,6-tetrahydropyridine (V) with b.p. 85° (2.5 mm). The picrate had m.p. 126-128° (from alcohol), and did not depress the melting point when mixed with the picrate of the dehydration product obtained from the γ-isomer of 1,2,5-trimethyl-4-phenyl-4-piperidol.

1-Acetyl-2,5-dimethyl-4-phenyl-4-piperidol (VI). a) Acetylation of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol. A solution of 1.8 ml of acetic anhydride in 5 ml of benzene was cautiously added with cooling to a mixture of 3 g of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (m.p. 121-122°) and 10 ml of anhydrous benzene. The reaction mixture was heated for one hour at benzene boil. The excess acetic anhydride, benzene and acetic acid were removed by distillation under a slight vacuum. The residue crystallized when absolute ether was added. The crystals were filtered and dried; weight 3.1 g, m.p. 104-106°. Two recrystallizations from gasoline gave 2.8 g of the γ-isomer of 1-acetyl-2,5-dimethyl-4-phenyl-4-piperidol (VI) with m.p. 108-110°.

Found %: N 5.86, 5.65. $C_{15}H_{21}O_2N$. Calculated %: N 5.67.

b) Acetylation of the α-isomer of 2,5-dimethyl-4-phenyl-4-piperidol. For reaction we took 1 g of the α-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (m.p. 163-166°), 1.3 ml of acetic anhydride and 10 ml of anhydrous benzene. A precipitate was obtained when the mixture was heated for 1.5 hours on the water bath, which was filtered and washed well with benzene. We obtained 1.1 g of crystals with m.p. 199-201°. After recrystallization from benzene the α-isomer of 1-acetyl-2,5-dimethyl-4-phenyl-4-piperidol (VI) melted at 200-202°.

Found %: N 5.64, 5.39. $C_{15}H_{21}O_2N$. Calculated %: N 5.67.

c) Phenylmagnesium bromide, prepared from 6 g of magnesium and 36 g of bromobenzene in 350 ml of ether, was added in two hours to a solution of 35 g of 1-acetyl-2,5-dimethyl-4-piperidone (XII) (m.p. 60-61°) in 200 ml of absolute ether. The next day, after heating for one hour, the reaction mixture was treated under cooling with 150 ml of saturated ammonium chloride solution. The ether layer was separated. In approximately an hour 11.7 g of a crystalline precipitate, with m.p. 173-176°, deposited from the ether layer. Recrystallization of the precipitate from anhydrous alcohol gave the third stereoisomeric form of 1-acetyl-2,5-dimethyl-4-phenyl-4-piperidol (VI) with m.p. 179-180°.

Found %: N 5.60, 5.98. $C_{15}H_{21}O_2N$. Calculated %: N 5.67.

Treatment of the water layer, saturated with ammonium chloride, with caustic, followed by extraction with ether, and distillation of the extracted products in vacuo gave 10.4 g of a viscous liquid with b.p. 117-119° (2.5 mm), which crystallized in the receiver. Recrystallization from ether gave 9.2 g of the starting 1-acetyl-2,5-dimethyl-4-piperidone (XII) with m.p. 56-58°.

In the experiments where either phenylmagnesium bromide or phenyllithium was reacted, not with the pure stereoisomer of 1-acetyl-2,5-dimethyl-4-piperidone with m.p. 60-61°, but instead with the mixture of stereoisomeric piperidones (XII), the same isomer of 1-acetyl-2,5-dimethyl-4-phenyl-4-piperidol with m.p. 179-180° was obtained.

d) The synthesis of 2,5-dimethyl-4-phenyl-4-piperidol (II) from 2,5-dimethyl-4-piperidone (I) and phenyllithium was described in the first experiment. A noncrystallizing oil remains after the crystalline γ- and α-isomers of piperidol (II) have been removed from the reaction products. A benzene solution of this residue (11.2 g) was heated for one hour with 16.3 g of acetic anhydride. The benzene and acetic anhydride were removed by distillation under a slight vacuum, and the residue was dissolved in absolute ether. After standing for some time the ether solution deposited 0.4 g of crystals with m.p. 170-174°, which after recrystallization from benzene melted at 188-179°, and failed to depress the melting point when mixed with the above-described specimen of 1-acetyl-2,5-dimethyl-4-phenyl-4-piperidol (VI).

γ-Isomer of 1-propionyl-2,5-dimethyl-4-phenyl-4-piperidol (VII). A solution of 1 g of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (II) in 10 ml of anhydrous benzene was treated with 1.4 ml of propionic anhydride. The mixture was heated for one hour. The benzene and excess propionic anhydride were vacuum-distilled. The residue was recrystallized from ether. We obtained 0.7 g of the γ-isomer of 1-propionyl-2,5-dimethyl-4-phenyl-4-piperidol (VII) with m.p. 81-83°.

Found %: N 5.43, 5.57. $C_{16}H_{23}O_2N$. Calculated %: N 5.36.

When a mixture of 2 g of the hydrochloride of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (m.p. 210-211°), 30 ml of propionic anhydride and 2 ml of propionyl chloride was heated on the boiling water bath for ten hours we obtained 1.6 g of 1-propionyl-2,5-dimethyl-4-phenyl-1,2,3,6-tetrahydropyridine as a viscous liquid with b.p. 173-174° (2.5 mm), n_D^{20} 1.5562.

Found %: N 6.15, 6.09. $C_{16}H_{21}ON$. Calculated %: N 5.76.

1-Benzoyl-2,5-dimethyl-4-phenyl-4-piperidol (VIII). Benzoyl chloride (5.8 g) was added gradually, with cooling and stirring, to 5 g of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (II) and a solution of 6 g of sodium hydroxide in 15 ml of water. The mixture was stirred for four hours at room temperature, and then extracted four times with 50 ml portions of ether. The reaction product after drying was vacuum-distilled. We obtained 2 g of a substance with b.p. 198° (2.5 mm), which crystallized when gasoline was added. Recrystallization from acetone gave 1.5 g of the γ-isomer of 1-benzoyl-2,5-dimethyl-4-phenyl-4-piperidol (VIII) with m.p. 187.5-188°.

Found %: N 4.33, 4.69. $C_{20}H_{23}O_2N$. Calculated %: N 4.53.

b) A solution of 70 g of mixed stereoisomeric 1-benzoyl-2,5-dimethyl-4-piperidones (XIII) in 200 ml of ether was added in four hours, with cooling and vigorous stirring, to the phenylmagnesium bromide obtained from 9 g of magnesium and 52 g of bromobenzene in 700 ml of ether. A copious white precipitate was obtained. After heating at ether boil for two hours, 500 ml of water was added. The ether layer was separated and dried over sodium sulfate. The residue after distilling off the ether was vacuum-distilled. The following fractions were obtained: first, 74-130° (3 mm), 6 g; second, 130-230° (3 mm), 45.7 g; third, 230-232° (2.5 mm), 19 g; residue 7 g.

From the first and second fractions, which crystallized in the receivers, we isolated 8.7 g of one of the stereoisomeric 1-benzoyl-2,5-dimethyl-4-piperidones (XIII) with m.p. 65.5-67.5°. From the third fraction by recrystallization from benzene we isolated 14 g of 1-benzoyl-2,5-dimethyl-4-phenyl-4-piperidol (VIII) with m.p. 89-94°.

Found %: N 3.94, 4.16. $C_{20}H_{23}O_2N$. Calculated %: N 4.53.

γ-Isomer of 1-diethylaminoacetyl-2,5-dimethyl-4-phenyl-4-piperidol (IX). A solution of 2 g of chloroacetyl chloride in 50 ml of benzene was added with stirring to a cooled to 0° solution of 7.5 g of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (II) in 100 ml of anhydrous benzene. The mixture was stirred for 1.5 hours at room temperature. The obtained precipitate was filtered, and washed well on the filter with benzene. We obtained 4 g of the hydrochloride of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol with m.p. 210-211° (from a mixture of acetone and alcohol).

Found %: N 5.20, 5.88. $C_{15}H_{20}O_2NCl$. Calculated %: N 5.79.

Removal of the solvent from the mother liquor by distillation gave 4.8 g of 1-chloroacetyl-2,5-dimethyl-4-phenyl-4-piperidol (XIV) as a yellow glass, which was dissolved in 15 ml of benzene and then added gradually to 5.7 g of diethylamine at the boiling point of the latter. Then the mixture was heated for another six hours. The benzene was distilled off. The residue was dissolved in 7 ml of water, treated with sodium hydroxide, and extracted with ether. Vacuum-distillation of the extracted products gave 2.1 g of a viscous liquid with b.p. 199-203° (2.5 mm), which crystallized when gasoline was added. We obtained colorless fine-grained crystals of the γ-isomer of 1-diethylaminoacetyl-2,5-dimethyl-4-phenyl-4-piperidol (IX) with m.p. 136-139°.

Found %: N 9.07, 8.78. $C_{19}H_{30}O_2N_2$. Calculated %: N 8.80.

γ-Isomer of 1-methylsulfonyl-2,5-dimethyl-4-phenyl-4-piperidol (X). A solution of 0.5 g of methanesulfonyl chloride in 10 ml of benzene was added in drops to a cooled solution of 1.75 g of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (II) in 15 ml of anhydrous benzene. The obtained precipitate (1.2 g) of the hydrochloride of piperidol (II) was filtered and washed with benzene. Removal of the benzene by distillation left 0.55 g of 1-methylsulfonyl-2,5-dimethyl-4-phenyl-4-piperidol (X), which after recrystallization from acetone had m.p. 168-170°.

Found %: N 4.76, 4.95. $C_{14}H_{21}O_3NS$. Calculated %: N 4.94.

γ-Isomer of 1-benzenesulfonyl-2,5-dimethyl-4-phenyl-4-piperidol (XI). For reaction we took 0.5 g of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (II), 1 g of 12% sodium hydroxide solution and 2.5 g of benzenesulfonyl chloride. The mixture was heated with stirring for nine hours on the water bath. The obtained precipitate was filtered and then recrystallized from anhydrous alcohol. We obtained 0.2 g of 1-benzenesulfonyl-2,5-dimethyl-4-phenyl-4-piperidol (XI) with m.p. 127-129°.

Found %: N 4.03, 4.02. $C_{19}H_{23}O_3NS$. Calculated %: N 4.06.

Action of hydrogen chloride on the γ- and α-isomers of 1-acetyl(propionyl)-2,5-dimethyl-4-phenyl-4-piperidol. a) A white precipitate was obtained when dry hydrogen chloride was passed into a solution of 0.2 g of the γ-isomer of 1-acetyl-2,5-dimethyl-4-phenyl-4-piperidol (VI) (m.p. 108-110°) in absolute ether, which after recrystallization from acetone gave 0.15 g of the hydrochloride of the acetate of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (XV) with m.p. 137-138°.

Found %: Cl 12.13; N 4.70, 4.80. $C_{15}H_{22}O_2NCl$. Calculated %: Cl 12.52; N 4.93.

A water solution of 0.5 g of the hydrochloride of the acetate of 2,5-dimethyl-4-phenyl-4-piperidol (XV) was treated with soda and ether. From the ether solution after drying we obtained 0.3 g of crystals with m.p. 109-110°, which failed to depress the melting point when mixed with the γ-isomer of 1-acetyl-2,5-dimethyl-4-phenyl-4-piperidol (VI).

b) A stream of dry hydrogen chloride was passed through a solution of 4 g of the γ-isomer of 1-propionyl-2,5-dimethyl-4-phenyl-4-piperidol (VII) (m.p. 81-83°) in absolute ether. The obtained precipitate of the hydrochloride of the propionate of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (XVI), after recrystallization from acetone, weighed 2.5 g and had m.p. 125-126°.

Found %: Cl 11.71; N 4.30, 4.54. $C_{16}H_{24}O_2NCl$. Calculated %: Cl 11.93; N 4.76.

When the propionate hydrochloride (XVI) in aqueous solution was treated with soda it reverted to the γ-isomer of 1-propionyl-2,5-dimethyl-4-phenyl-4-piperidol (VII) with m.p. 81-83°.

c) Dry hydrogen chloride (4.3 g) was passed into a hot solution of 0.8 g of the α-isomer of 1-acetyl-2,5-dimethyl-4-phenyl-4-piperidol (VI) (m.p. 200-202°) in 80 ml of anhydrous dioxane. A white precipitate deposited in two days, which after recrystallization from acetone gave 0.6 g of the hydrochloride with m.p. 136-138°, and not depressing the melting point when mixed with the hydrochloride of the acetate of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol (XV). A water solution of 0.3 g of the 2,5-dimethyl-4-phenyl-4-piperidol acetate hydrochloride (XV) was treated with soda and ether. From the ether solution after drying we obtained 0.1 g of crystals with m.p. 108-109°, which did not depress the melting point when mixed with the γ-isomer of 1-acetyl-2,5-dimethyl-4-phenyl-4-piperidol (VI).

1-Acetyl-2,5-dimethyl-4-phenyl-4-bromo(chloro)-piperidine. a) The γ-isomer of 1-acetyl-2,5-dimethyl-4-phenyl-4-piperidol (VI) (m.p. 108-110°) (0.5 g) was dissolved in 3.5 ml of freshly distilled acetyl bromide. Within five minutes a precipitate of the hydrobromide of the acetate of the γ-isomer of 2,5-dimethyl-4-phenyl-4-piperidol with m.p. 130-130.5° was obtained (0.3 g). When treated with an aqueous solution of soda it reverted to the original γ-isomer of piperidol (VI). Partial removal of acetyl bromide from the mother liquor, remaining after separation of the acetate hydrobromide, led to obtaining 0.1 g (after recrystallization from acetone) of 1-acetyl-2,5-dimethyl-4-phenyl-4-bromopiperidine (XVII) with m.p. 159-161°.

Found %: C 57.82, 58.13; H 6.40, 6.44; N 4.36, 4.42; Br 26.13, 25.59. $C_{15}H_{20}ONBr$. Calculated %: C 58.01; H 6.45; N 4.51; Br 25.80.

b) The α-isomer of 1-acetyl-2,5-dimethyl-4-phenyl-4-piperidol (VI) (m.p. 200-202°) (0.5 g) was dissolved in 3.5 ml of acetyl bromide. After one hour the excess acetyl bromide was vacuum-distilled. From the residue after two recrystallizations from acetone we obtained 0.3 g of 1-acetyl-2,5-dimethyl-4-phenyl-4-bromopiperidine (XVIII) with m.p. 153-154°, and failing to depress the melting point when mixed with the same product, obtained from the γ-isomer of piperidol (VI).

c) A mixture of 1 g of the γ-isomer of 1-acetyl-2,5-dimethyl-4-phenyl-4-piperidol (VI) (m.p. 108-110°) and 0.6 ml of acetyl chloride was heated in benzene solution in the presence of 0.2 g of magnesium metal for 16 hours. After removal of the solvent and acetyl chloride by distillation, the residue was washed with ether, and then recrystallized from benzene. We obtained 0.2 g of 1-acetyl-2,5-dimethyl-4-phenyl-4-chloropiperidine as colorless crystals with m.p. 143-146°. It failed to change when kept in the air.

Found %: N 5.30, 5.43. $C_{15}H_{20}ONCl$. Calculated %: N 5.27.

1-Acetyl-2,5-dimethyl-4-phenyl-1,2,3,6-tetrahydropyridine (XVIII). a) A water solution of 0.5 g of 1-acetyl-2,5-dimethyl-4-phenyl-4-bromopiperidine (XVII) was treated first with 8% soda solution and then with ether. From the ether extract, after drying over sodium sulfate and removal of the ether by distillation, we obtained 0.3 g of 1-acetyl-2,5-dimethyl-4-phenyl-1,2,3,6-tetrahydropyridine (XVIII) as colorless crystals with m.p. 65-67° (from gasoline).

Found %: N 6.41, 6.08. $C_{15}H_{19}ON$. Calculated %: N 6.11.

b) A mixture of 1 g of 2,5-dimethyl-4-phenyl-1,2,3,6-tetrahydropyridine (IV) and 1.6 ml of acetic anhydride in 5 ml of anhydrous benzene was heated on the boiling water bath for 1.5 hours. The acetic anhydride was vacuum-distilled, and the residue was dissolved in water, neutralized with soda solution, and extracted with ether. From the ether solution we obtained 0.6 g of 1-acetyl-2,5-dimethyl-4-phenyl-1,2,3,6-tetrahydropyridine (XVIII) with m.p. 67-78° (from gasoline), which did not depress the melting point when mixed with the above-described specimen of this product.

1-Acetyl-2,5-dimethyl-4-phenyl-4,5-dibromopiperidine (XIX). A solution of 0.11 ml of bromine in 5 ml of carbon tetrachloride was added slowly and with cooling to a solution of 0.5 g of 1-acetyl-2,5-dimethyl-1,2,3,6-tetrahydropyridine (IV) in 10 ml of carbon tetrachloride. The obtained orange precipitate was separated, washed thoroughly with gasoline, and dried. We obtained 0.5 g of 1-acetyl-2,5-dimethyl-4-phenyl-4,5-dibromopiperidine (XIX), which deliquesces in the air. The compound changed to an oil when heated to 38°.

Found %: N 3.28, 3.32. $C_{15}H_{19}ONBr$. Calculated %: N 3.59.

SUMMARY

2,5-Dimethyl-4-phenyl-4-piperidol was synthesized. From the corresponding isomers of this alcohol we obtained the stereoisomeric 1,2,5-trimethyl-4-phenyl-4-piperidols and 1-acyl-2,5-dimethyl-4-phenyl-4-piperidols. In a number of cases (during dehydration, action of hydrogen chloride, treatment with acetyl bromide) we observed a conversion of the α-isomer of the piperidol to the γ-isomer.

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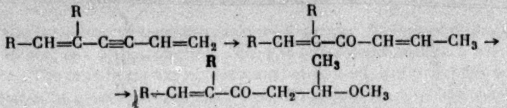
ACETYLENE DERIVATIVES

CXCIV. HYDRATION OF DIVINYLACETYLENE AND VINYLISOPROPENYLACETYLENE IN ALCOHOL SOLUTIONS

I.N. Nazarov,* S.A. Vartanian and S.G. Matsoian

Based on numerous examples it was shown in our laboratory that divinylacetylenic hydrocarbons, when heated in aqueous methanol solution in the presence of sulfuric acid and mercuric sulfate, are easily hydrated with the formation of the corresponding dienones. In all cases the water adds in such manner that the oxygen is found on the carbon atom attached to the substituted vinyl radical.

It was established that the hydration rate depends on the structure of the dienyne. Divinylacetylene itself and the symmetrically substituted dienynes are hydrated with the greatest difficulty. The introduction of one, and especially of two, substituents in one of the vinyl radicals of the dienyne (not symmetrical substitution) greatly accelerates the hydration reaction. The hydration rate again decreases as the size of the substituent is increased. The dienones formed under the reaction conditions add the elements of methyl alcohol and are converted to β-methoxy ketones.

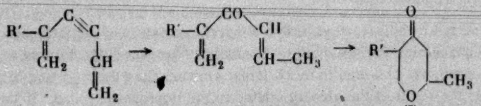


$$R-CH=\overset{R}{C}-C\equiv C-CH=CH_2 \rightarrow R-CH=\overset{R}{C}-CO-CH=CH-CH_3 \rightarrow R-CH=\overset{R}{C}-CO-CH_2-\overset{CH_3}{CH}-OCH_3$$

The addition of methyl alcohol proceeds in such manner that the methoxyl group is always found in the β-position to the carbonyl group [1].

It seemed of interest to determine if it was possible to hydrate dienynes in the presence of other alcohols, which would permit obtaining various β-alkoxy ketones. It proved that, depending on the conditions used, this reaction leads to the formation of either the corresponding β-alkoxy ketones or to tetrahydro-γ-pyrones. The ease and the time needed to hydrate dienynes also depend on the nature of the alcohol; the hydration rate decreases with branching and increase in the molecular weight of the alcohol.

The corresponding tetrahydro-γ-pyrones are obtained in 50% yield when divinylacetylene and vinylisopropenylacetylene are heated in a 50-60% aqueous solution of either ethyl or methyl alcohol, in the presence of mercuric sulfate and sulfuric acid [1, 2].



R' = H, CH₃

(I)

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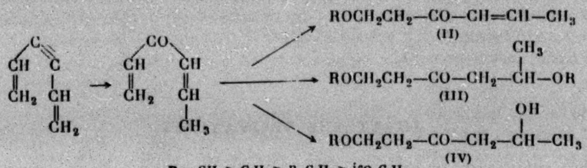
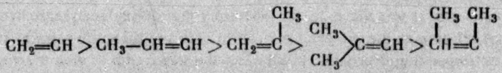
* Deceased.

The hydration of divinylacetylene in 80-95% alcohol solutions gives, together with pyrone (I), also substantial amounts of a mixture of the three alkoxy ketones (II-IV).



$R = CH_3 > C_2H_5 > n\text{-}C_4H_9 > iso\text{-}C_3H_7.$

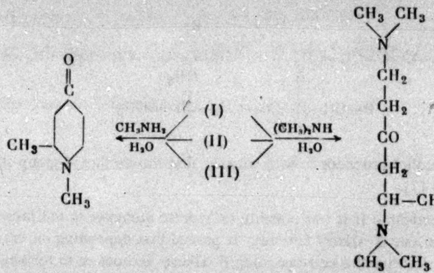
The addition of alcohols proceeds more rapidly at the vinyl radical of vinyl propenyl ketone, and in accordance with this the monomethoxy ketones (II) are formed in the larger amounts. The rate with which alcohols (and also amines and other compounds) add to the vinyl radicals of α,β-unsaturated ketones decreases in the following order:



$$CH_2{=}CH > CH_3{-}CH{=}CH > CH_2{=}C(CH_3) > (CH_3)_2C{=}CH > CH(CH_3){=}C(CH_3)$$

A disubstituted vinyl group proves to be incapable of adding alcohols (even methanol) [3]. The propenyl group adds alcohols more readily than does the isopropenyl group, while the unsubstituted vinyl group shows the easiest additions of all.

The reaction of either aqueous methylamine or dimethylamine solution with ketones (I-IV) yields, as the result of ammonolysis, either 1,2-dimethyl-4-piperidone (V) [4] or 1,5-bis(dimethylamino)-3-hexanone (VI).

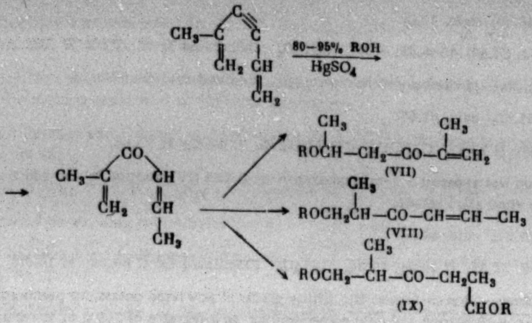


(V) (VI)

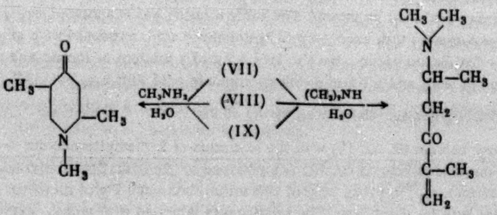
On hydrolysis with 10% sulfuric acid the alkoxy ketones (II-IV) are converted to 2-methyltetrahydro-γ-pyrone (I).

The main reaction products when vinylisopropenylacetylene [6] is hydrated in 80-95% alcohol solutions are the corresponding β-alkoxy ketones (VII-IX).

In the case of primary alcohols (methyl, ethyl, n-butyl) a mixture of all three alkoxy ketones (VII, VIII, IX) is formed, in which connection the low-boiling monoalkoxy ketones (VII), formed as the result of the alcohol adding to the propenyl group, are obtained in much larger amounts than the isomeric high-boiling monoalkoxy ketones (VIII), formed as the result of the alcohol adding to the isopropenyl group. If the hydration of vinylisopropenylacetylene is run in isopropyl alcohol solution, then the solitary reaction product is the monoalkoxy ketone (VII, R = iso-C_3H_7), and, consequently, isopropyl alcohol already proves to be completely incapable of adding to the isopropenyl group of propenyl isopropenyl ketone. The reaction of either aqueous methylamine or dimethylamine with ketones (VII, VIII, IX) gave, respectively, as the result of ammonolysis, either 1,2,5-trimethyl-4-piperidone [4] or 2-dimethylamino-5-methyl-5-hexan-4-one [5] in good yields.



$R = CH_3 > C_2H_5 > iso\text{-}C_3H_7 > n\text{-}C_4H_9$



EXPERIMENTAL

Hydration of divinylacetylene to 2-methyltetrahydro-4-pyrone. Divinylacetylene (100 g) was added dropwise in 18 hours with stirring to a boiling mixture of 200 g of 50% aqueous methanol, 3 ml of sulfuric acid and 3 g of mercuric sulfate. The experiment was run for a total of 40 hours, and during this time another 21 g of mercuric sulfate (a total of 24 g) was added in small portions. Most of the methanol was distilled off, while the product was salted out with potash, extracted with ether, dried over sodium sulfate, and then fractionally distilled. We obtained 62 g of 2-methyltetrahydro-4-pyrone (I) with b.p. 65-68° (15 mm), n_D^{20} 1.4440. The semicarbazone had m.p. 169° and did not depress the melting point when mixed with an authentic specimen.

We recovered 23 g of divinylacetylene from the distilled alcohol. When the experiment was repeated in 50% ethyl alcohol we obtained a lower yield of 2-methyltetrahydro-4-pyrone.

Hydration of divinylacetylene in ethyl alcohol. A mixture of 860 g of 80% ethanol, 5 ml of concentrated sulfuric acid, 3 g of mercuric sulfate and 200 g of divinylacetylene (b.p. 80-83°, n_D^{20} 1.5000) was vigorously stirred at 78-82° for 35 hours. Here small portions of catalyst were added every two hours, and in this way another 48 g of mercuric sulfate was added. Most of the alcohol was distilled off under a slight vacuum, and when it was fractionally distilled at atmospheric pressure we recovered 27 g of divinylacetylene. The reaction mass was neutralized with soda, extracted with ether, dried over sodium sulfate, and fractionally distilled in vacuo. We obtained 136 g of hydration products with b.p. 69-103° (13 mm), n_D^{20} 1.4480, and about 36 g of a tarry residue. Fractional distillation of 200 g of the described hydration products of divinylacetylene, obtained from several experiments, gave the following fractions: 1st, 68-70° (13 mm), n_D^{20} 1.4440, 48 g; 2nd, 98-100° (13 mm), n_D^{20} 1.4419, 31 g; 3rd, 106-108° (11 mm), n_D^{20} 1.4305, 57.2 g; 4th, 115-117° (12 mm), n_D^{20} 1.4435, 5.3 g. We obtained 30.5 g of an intermediate fraction.

The first fraction was 2-methyltetrahydro-4-pyrone (I), the semicarbazone of which had m.p. 169-170°, and did not give a melting point depression with an authentic specimen.

The second fraction was 1-ethoxy-4-hexen-3-one (II), obtained as a mobile yellow liquid.

d_4^{20} 0.9240, MR 40.70; calc. 40.33.

Found %: C 67.91, 67.87; H 10.09, 10.05. $C_8H_{14}O_2$. Calculated %: C 67.60; H 9.86.

The third fraction was 1,5-diethoxy-3-hexanone (III), obtained as a clear liquid.

d_4^{20} 0.9508, MR 51.62; calc. 51.67.

Found %: C 63.87; H 10.67. $C_{10}H_{20}O_2$. Calculated %: C 63.83; H 10.64.

The fourth fraction was apparently 1-ethoxyhexan-5-ol-3-one (IV), formed by the addition of a molecule of ethanol and water to vinyl allyl ketone.

d_4^{20} 0.9996, MR 42.51; calc. 42.32.

Found %: C 59.69, 59.53; H 10.34, 10.34. $C_8H_{16}O_3$. Calculated %: C 60.00; H 10.00.

Oxidation of 1-ethoxy-4-hexen-3-one (II). Thirty grams of powdered potassium permanganate was gradually added in four hours, with stirring and cold-water cooling, to a mixture of 200 g of water and 8 g of ethoxy ketone (II) (b.p. 98-100° at 13 mm, n_D^{20} 1.4413), and then the stirring was continued for another four hours at room temperature. The manganese dioxide was filtered and washed with hot water. The presence of neutral products in the ether extract could not be shown. The water solution was evaporated to dryness on the water bath, and the residue of salts was treated with concentrated hydrochloric acid, extracted with ether, dried over sodium sulfate, and fractionally distilled in vacuo. We obtained 1.7 g of a mixture of formic and acetic acids with b.p. 98-106° (680 mm) (calomel test), and 2.1 g of β-ethoxypropionic acid with b.p. 141-143° (28 mm), n_D^{20} 1.4230.

Found %: Ag 47.93. $C_5H_9O_2Ag$. Calculated %: Ag 48.00.

Hydrolysis of ethoxy ketones (II, III, IV) with the formation of 2-methyltetrahydro-4-pyrone (I). Ten grams of the above-described mixture of ketones (II, III, IV), obtained by the hydration of divinylacetylene in ethyl alcohol (b.p. 65-110° at 12 mm, n_D^{20} 1.4470), 25 g of 10% sulfuric acid and 1 g of mercuric sulfate were stirred with heating on the water bath for four hours. The solution was saturated with potash, extracted with ether, the extract dried over sodium sulfate, and the product fractionally distilled in vacuo. We isolated 4.3 g of 2-methyltetrahydro-4-pyrone with b.p. 60-62° (15 mm), n_D^{20} 1.4440.

The semicarbazone had m.p. 169-170° and did not depress the melting point with an authentic specimen.

Reaction of methylamine with ethoxy ketones (II-IV). A mixture of 15 g of ethoxy ketones (b.p. 65-100° at 12 mm, n_D^{20} 1.4470), 23 g of 24% aqueous methylamine solution and 10 ml of alcohol was heated in a glass ampoule at 65-70° for three hours. The solution was acidified with dilute hydrochloric acid, and the neutral products were extracted with ether, but after distilling off the ether they proved to be present in very small amount. The organic bases were salted out with potash, extracted with ether, dried over sodium sulfate, and fractionally distilled in vacuo. We obtained 6.8 g of the earlier-described [4] 1,2-dimethyl-4-piperidone (V) with b.p. 80-82° (10 mm), n_D^{20} 1.4583. The picrate had m.p. 163-164°, and did not depress the melting point with an authentic specimen.

Reaction of dimethylamine with ethoxy ketones (II-IV). A mixture of 10 g of ethoxy ketones (b.p. 65-110° at 12 mm, n_D^{20} 1.4470) and 23 g of a 25% aqueous dimethylamine solution was heated at 70° for three hours. Then the excess dimethylamine was vacuum-distilled on the water bath at 45°. The residue was acidified with dilute hydrochloric acid, extracted with ether, and after distilling off the ether we obtained a total of about 1 g of neutral products. The water solution was saturated with potash, the bases extracted with ether, the extract dried over sodium sulfate, and the product fractionally distilled in vacuo. We obtained 3.4 g of 1,5-bis(dimethylamino)-3-hexanone (VI) with b.p. 85-87° (9 mm), n_D^{20} 1.4560. The picrate had m.p. 145-146°, and did not depress the melting point with an authentic specimen.

Hydration of divinylacetylene in butanol. A mixture of 250 g of divinylacetylene and 90 g of water was added dropwise in 20 hours with constant stirring to a heated to 95° mixture of 500 g of butyl alcohol, 5 ml of sulfuric acid and 5 g of mercuric sulfate. Stirring at 95-100° was continued for another 48 hours, and during this time 42 g of mercuric sulfate was added in portions. The reaction mixture was neutralized with potash, filtered, and the butyl alcohol vacuum-distilled on the water bath. The residue was extracted with ether, dried over sodium sulfate, and vacuum-distilled. We obtained 105 g of hydration products with b.p. 73-113° (12 mm), n_D^{20} 1.4543. We took 153 g of this mixture, obtained from two experiments, and fractionally distilled in vacuo.

The following fractions were obtained: 1st, 73-75° (30 mm), n_D^{20} 1.4440, 37 g; 2nd, 100-102° (11 mm), n_D^{20} 1.4610, 31 g; 3rd, 135-137° (11 mm), n_D^{20} 1.4313, 12.5 g. We also collected 48.5 g of intermediate fractions.

The first fraction was 2-methyltetrahydro-4-pyrone (I), the semicarbazone of which had m.p. 169°, and did not depress the melting point with an authentic specimen.

The second fraction was 1-butoxy-4-hexen-3-one (II, R = C_4H_9), obtained as a yellowish liquid, d_4^{20} 0.9236, MR 50.52; calc. 49.55.

Found %: C 70.28; H 10.33. $C_{10}H_{18}O_2$. Calculated %: C 70.59; H 10.59.

The compound on standing polymerizes first to a viscous, and then to a hard brittle mass.

The third fraction was 1,5-dibutoxy-3-hexanone (III, R = C_4H_9), obtained as a colorless liquid. d_4^{20} 0.9089, MR 70.03; calc. 69.65.

Found %: C 68.60; H 10.86. $C_{14}H_{28}O_3$. Calculated %: C 68.85; H 11.48.

Reaction of methylamine with butoxy ketones (II-IV). A mixture of 10 g of butoxy ketones (II, III, IV, R = C_4H_9) (b.p. 90-135° at 11 mm, n_D^{20} 1.4550), 25 g of a 24% aqueous methylamine solution and 20 ml of alcohol was heated in a glass ampoule on the water bath at 70° for three hours. The excess methylamine was distilled on the water bath at 50° (70 mm), the solution was acidified with dilute hydrochloric acid, and the neutral products were extracted with ether to subsequently give 2.7 g of butyl alcohol with b.p. 115°. The organic bases were salted out with potash, extracted with ether, dried over sodium sulfate, and vacuum-distilled. We obtained 2.3 g of 1,2-dimethyl-4-piperidone with b.p. 78-80° (9 mm), n_D^{20} 1.4580. The picrate had m.p. 163-164°, and did not depress the melting point with an authentic specimen.

Hydration of vinylisopropenylacetylene to 2,5-dimethyltetrahydro-4-pyrone. Vinylisopropenylacetylene [2] (b.p. 40-43° at 40 mm, n_D^{20} 1.4950) (100 g) was added dropwise in 16 hours, with stirring, to a boiling mixture of 200 g of 50% methanol, 3 ml of sulfuric acid and 3 g of mercuric sulfate. Then the heating and stirring was continued for another 18 hours, and during this time another 13 g of mercuric sulfate was added in small portions. The whole experiment lasted 34 hours. The total amount of mercuric sulfate added was 16 g. Most of the methanol was distilled off, while the product was salted out with potash, extracted with ether, dried over sodium sulfate, and fractionally distilled. We obtained 72 g of a hydration product with b.p. 80-83° (40 mm) and n_D^{20} 1.4466. Redistillation at atmospheric pressure gave the following fractions: 1st, 164-166° (680 mm), n_D^{20} 1.4459, 13 g; 2nd, 171-173° (680 mm), n_D^{20} 1.4486, 25 g; 3rd, 180-185° (680 mm), n_D^{20} 1.4476, 15 g.

The first fraction was 1,3-dimethyl-1-cyclopenten-5-one (the semicarbazone had m.p. 172-173°) with some 2,5-dimethyltetrahydro-4-pyrone as impurity.

The second fraction was 2,5-dimethyltetrahydro-4-pyrone.

B.p. 171-173° (680 mm), n_D^{20} 1.4486, d_4^{20} 1.0190, MR 33.70; calc. 33.98.

Found %: C 65.83; H 10.15. $C_7H_{12}O_2$. Calculated %: C 65.52; H 9.38.

The semicarbazone of 2,5-dimethyltetrahydro-4-pyrone had m.p. 169.5-170.5°.

The third fraction was 1,3-dimethyl-3-cyclopenten-5-one (the semicarbazone had m.p. 190-191°) with some 2,5-dimethyltetrahydro-4-pyrone as impurity.

Hydration of vinylisopropenylacetylene in ethyl alcohol. A mixture of 1000 ml of ethyl alcohol, 250 ml of water, 15 ml of sulfuric acid, 5 g of mercuric sulfate and 250 g of vinylisopropenylacetylene (b.p. 45° at 50 mm, n_D^{20} 1.4962) was vigorously stirred at 78-83° for 32 hours. During this time another 32 g of mercuric sulfate (a total of 37 g) was added in small portions. Then the mixture was neutralized with soda, filtered, the alcohol distilled off, and the product extracted with ether, dried over sodium sulfate, and fractionally distilled in vacuo. We obtained 179 g of a mixture of 2,5-dimethyltetrahydro-4-pyrone and ethoxy ketones (VII, VIII, IX) with b.p. 80-114° (12 mm). The tarry residue from the distillation weighed 32 g.

From the distilled alcohol we recovered 35 g of vinylisopropenylacetylene with b.p. 40-42° (41 mm) and n_D^{20} 1.4956.

After repeated fractional distillation of the hydration products in vacuo we isolated the following fractions:

1st, 80-82° (40 mm), n_D^{20} 1.4487, 50 g; 2nd, 76-77° (11 mm), n_D^{20} 1.4460, 80 g; 3rd, 98-100° (11 mm), n_D^{20} 1.4500, 13 g; 4th, 110-112° (12 mm), n_D^{20} 1.4320, 10.5 g.

The first fraction was 2,5-dimethyltetrahydro-4-pyrone with some of the 1,3-dimethylcyclopentenone as impurity. The semicarbazone had m.p. 169.5-170.5°, and did not depress the melting point with the above-described process.

The second fraction was 2-ethoxy-5-methyl-5-hexen-4-one (VII), obtained as a mobile liquid.

d_4^{20} 0.9370, MR 45.80; calc. 44.95.

Found %: C 69.60; H 10.50. $C_9H_{16}O_2$. Calculated %: C 69.23; H 10.02.

We were unable to obtain a crystalline derivative with 2,4-dinitrophenylhydrazine.

The third fraction was 1-ethoxy-2-methyl-5-hexen-3-one (VIII), obtained as a light-yellow mobile liquid.

d_4^{20} 0.9205, MR 45.80; calc. 44.95.

Found %: C 69.78; H 10.30. $C_9H_{16}O_2$. Calculated %: C 69.23; H 10.02.

The fourth fraction was 1,5-diethoxy-2-methyl-3-hexanone (IX), obtained as a colorless mobile liquid.

d_4^{20} 0.9450, MR 55.82; calc. 56.28.

Found %: C 64.61; H 10.71. $C_{11}H_{22}O_3$. Calculated %: C 65.34; H 10.89.

Oxidation of 2-ethoxy-5-methyl-4-hexen-4-one (VII). Powdered potassium permanganate (27 g) was added gradually in four hours, with stirring and ice-water cooling, to 9 g of the ethoxy ketone (b.p. 85-87° at 15 mm, n_D^{20} 1.4454) in 100 ml of water. The manganese dioxide was filtered and washed with hot water. The water solution was extracted with ether, and then evaporated on the water bath to dryness. The residue of salts was acidified with 13 ml of concentrated hydrochloric acid and then thoroughly extracted with ether. The ether was removed by distillation and the mixed acids were fractionally distilled in vacuo. The following fractions were collected: 1st, 45-48° (22 mm), n_D^{20} 1.3869, 1.1 g; 2nd, 48-108° (20 mm), n_D^{20} 1.4109, 0.4 g; 3rd, 108-109° (19 mm), n_D^{20} 1.4270, 1.5 g.

The first fraction was a mixture of formic and acetic acids, which reduced a solution of mercuric chloride. The silver salts of acetic acid were obtained by fractional precipitation.

Found %: Ag 64.73, 64.55. $C_2H_3O_2Ag$. Calculated %: Ag 64.66.

The third fraction was β-ethoxybutyric acid (b.p. 108-109° at 19 mm, n_D^{20} 1.4270).

Removal of the ether by distillation failed to yield any neutral products.

Oxidation of 1-ethoxy-2-methyl-4-hexen-3-one. Powdered potassium permanganate (35 g) was added gradually in five hours, with stirring, at +10°, to a mixture of 14.2 g of the ketone (b.p. 95-98° at 15 mm, n_D^{20} 1.4486) and 150 ml of water. The manganese dioxide was filtered and washed with hot water. The water solution was extracted with ether to remove neutral products, and then it was evaporated on the water bath to dryness. The residue of salts was acidified with 23 ml of concentrated hydrochloric acid, then thoroughly extracted with ether, and after distilling off the ether the acids were fractionally distilled in vacuo. We obtained 1.7 g of formic acid with b.p. 49.51° (28 mm), 98-101° (680 mm), n_D^{20} 1.3863 (reduces a solution of mercuric chloride), and 2.3 g of β-ethoxymethacrylic acid with b.p. 119-120° (24 mm), n_D^{20} 1.4269.

Reaction of methylamine with ethoxy ketones (VII-IX). A mixture of 12 g of the above-described ethoxy ketones (b.p. 80-100° at 11 mm, n_D^{20} 1.4482) and 28 g of a 25% aqueous methylamine solution was heated in a metal ampoule at 70° for 3.5 hours. The excess methylamine was distilled on the water bath at 45° and a vacuum of 70 mm, the solution acidified with hydrochloric acid until weakly acid, and the neutral products, which proved to be present only in trace amount, were extracted with ether. The organic bases were salted out with potash, extracted with ether, dried over sodium sulfate, and fractionally distilled in vacuo.

We obtained 7.2 g of 1,2,3-trimethyl-4-piperidone with b.p. 76-77° (8 mm) and n_D^{20} 1.4565. The picrate had m.p. 161-162°, and did not depress the melting point with an authentic specimen [4].

Reaction of dimethylamine with ethoxy ketones (VII-IX). A mixture of 15 g of mixed ethoxy ketones (b.p. 80-110° at 11 mm, n_D^{20} 1.4482) and 40 g of a 24% aqueous dimethylamine solution was heated in a glass ampoule on the boiling-water bath for four hours. The excess dimethylamine was removed in vacuo on the water bath at 50°. The solution was acidified with hydrochloric acid until weakly acid, and the neutral products were extracted with ether. The organic bases were salted out with potash, extracted with ether, dried over Na_2SO_4, and fractionally distilled in vacuo. We obtained 9.3 g of the earlier-described 2-methyl-5-dimethylamino-2-hexen-3-one [4] with b.p. 80-82° (6 mm), n_D^{20} 1.4560. The picrate had m.p. 125°, and did not depress the melting point with an authentic specimen [5].

Hydration of vinylisopropenylacetylene in isopropyl alcohol. A mixture of 600 g of isopropyl alcohol, 80 ml of water, 5 ml of sulfuric acid, 200 g of vinylisopropenylacetylene (b.p. 45° at 50 mm, n_D^{20} 1.4960) and 12 g of mercuric sulfate was heated at 70° for 20 hours. Then 150 ml of acetone was added to obtain a homogeneous solution, and the stirring at mixture-boil continued for 26 hours. During this time another 19 g of mercuric sulfate (a total of 31 g) was added in small portions. The reaction product was neutralized with potash and filtered. Most of the isopropyl alcohol was vacuum-distilled on the water bath at 60°, while the product was extracted with ether, dried over sodium sulfate, and fractionally distilled. We obtained 63 g of recovered dienyne (b.p. 45-46° at 45 mm, n_D^{20} 1.4960) and 57 g of 2-isopropoxy-5-methyl-5-hexen-4-one (VII, R = iso-C_3H_7) as a pale-yellow liquid.

B.p. 79-81° (14 mm), n_D^{20} 1.4620, d_4^{20} 0.9340, MR 50.20; calc. 49.58.

Found %: C 70.36, 70.33; H 10.38, 10.77. $C_{10}H_{18}O_2$. Calculated %: C 70.59; H 10.59.

Hydration of vinylisopropenylacetylene in butanol. A mixture of 190 g of vinylisopropenylacetylene and 80 ml of water was added dropwise in 20 hours, with constant stirring, to a heated to 90° mixture of 500 g of butyl alcohol (b.p. 115°), 5 ml of sulfuric acid and 5 g of mercuric sulfate. Stirring at 90-100° was continued for 40 hours, and during this time another 30 g of mercuric sulfate was added in small portions. The product was neutralized with potash, filtered, the butyl alcohol vacuum-distilled on the water bath, and the residue extracted with ether, dried over sodium sulfate, and fractionally distilled. We obtained 108 g of a mixture of hydration products with b.p. 53-151° (18 mm) and n_D^{20} 1.4480. From the distilled butanol we isolated another 45 g of starting dienyne with b.p. 46-48° (50 mm) and n_D^{20} 1.4955. We took 203 g of the above-described mixture of hydration products, obtained from two similar experiments, and after fractional distillation in vacuo collected the following fractions: 1st, 86-88° (41 mm), n_D^{20} 1.4480, 33 g; 2nd, 95-97° (11 mm), n_D^{20} 1.4630, 45 g; 3rd, 111-112° (11 mm), n_D^{20} 1.4560, 15 g; 4th, 145-147° (11 mm), n_D^{20} 1.4350, 10 g. We also collected 63 g of intermediate fractions.

The first fraction was 2,5-dimethyltetrahydro-4-pyrone with some 1,3-dimethylcyclopentanone as impurity. The semicarbazone had m.p. 169.5-170.5°, and did not depress the melting point with an authentic specimen.

The second fraction, a pale-yellow liquid, was 2-butoxy-5-methyl-5-hexen-4-one (VII, R = C_4H_9).

B.p. 95-97° (11 mm), n_D^{20} 1.4630, d_4^{20} 0.9240, MR 54.83; calc. 54.20.

Found %: C 71.34, 71.12; H 10.90, 10.90. $C_{11}H_{20}O_2$. Calculated %: C 71.74; H 10.86.

The third fraction, a yellowish liquid, was 1-butoxy-2-methyl-4-hexen-3-one (VIII, R = C_4H_9).

B.p. 111-112° (11 mm), n_D^{20} 1.4560, d_4^{20} 0.9024, MR 55.00; calc. 54.20.

Found %: C 71.44, 71.07; H 10.99, 10.78. $C_{11}H_{20}O_2$. Calculated %: C 71.74; H 10.86.

The fourth fraction, a clear liquid, was 1,5-dibutoxy-5-methyl-3-hexanine (IX).

B.p. 145-147° (11 mm), n_D^{20} 1.4350, d_4^{20} 0.9105, MR 73.40; calc. 74.62.

Found %: C 70.27, 70.10; H 11.34, 11.65. $C_{15}H_{30}O_3$. Calculated %: C 70.30; H 11.72.

The butoxy ketones (VII, VIII, XI, R = C_4H_9) failed to give crystalline derivatives with 2,4-dinitrophenylhydrazine.

Reaction of methylamine with butoxy ketones (VII-IX). A mixture of 10 g of the butoxy ketone (b.p. 96-112° at 11 mm, n_D^{20} 1.4560), 25 g of a 24% aqueous methylamine solution and 30 ml of alcohol was heated in a glass ampoule on the boiling-water bath for four hours. The excess methylamine was distilled in vacuo (70 mm) on the water bath at 50°. The solution was acidified with dilute hydrochloric acid, and the neutral products were extracted with ether. We obtained 3 g of butyl alcohol with b.p. 115°. The organic bases were salted out with potash, extracted with ether, dried over sodium sulfate, and vacuum-distilled. We obtained 3.2 g of 1,2,5-trimethyl-4-piperidone with b.p. 70-72° (7 mm), n_D^{20} 1.4563. The picrate had m.p. 161-162° (from alcohol), and did not depress the melting point with an authentic specimen [4].

Hydration of vinylisopropenylacetylene in methyl alcohol. Water (45 ml) was added dropwise in eight hours, with stirring, to a boiling mixture of 100 g of the dienyne (b.p. 51-53° at 43 mm, n_D^{20} 1.4949), 100 g of methyl alcohol, 3 ml of sulfuric acid and 3 g of mercuric sulfate, and during this time another 8 g of mercuric sulfate was added in small portions. At reaction end (8 hours) the odor of the dienyne had disappeared. The mixture was treated with 50 ml of water, and the reaction product was extracted with ether, washed with soda solution, dried over sodium sulfate, and fractionally distilled in vacuo. We obtained 86 g of mixed methoxy ketones with b.p. 64-97° (12 mm), n_D^{20} 1.4463 [1].

SUMMARY

1. Divinylacetylene and vinylisopropenylacetylene, when heated in aqueous solutions of ethanol, butanol and isopropyl alcohol in the presence of mercuric sulfate and sulfuric acid, suffer hydration to the corresponding dienones. Here divinylacetylene gives vinyl propenyl ketone, while vinylisopropenylacetylene gives propenyl isopropenyl ketone. The resulting dienones under the reaction conditions add either one or two molecules of the alcohol and are converted to the corresponding β-alkoxy ketones; the yield of these ketones decreases with increase in the molecular weight of the alcohol.

2. The hydration of divinylacetylene in either 50% methyl or ethyl alcohol gives 2-methyltetrahydro-4-pyrone as the solitary reaction product in a yield of 50%.

Alcohols add to dienones in such manner that the alkoxy group is always found in the β-position to the carbonyl group.

3. All of the β-alkoxy ketones synthesized by us are capable of reacting with primary and secondary amines to yield, depending on the reaction conditions, either 4-piperidones or β-amino ketones.

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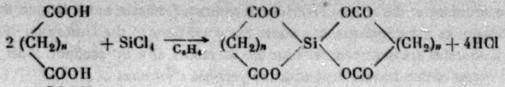
TETRAACYLOXYSILANES IN ORGANIC SYNTHESIS

XVIII. STRUCTURE OF THE SILICOANHYDRIDES OF DIBASIC SATURATED ORGANIC ACIDS

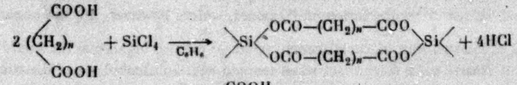
Iu.K. Iur'ev, Z.V. Beliakova and G.B. Eliakov

In previous papers we had shown that silicon tetrachloride reacts with dibasic saturated organic acids in a neutral solvent (benzene) with the liberation of hydrogen chloride and the formation of silicoanhydrides of the dibasic organic acids. The latter (silicoanhydrides) in the presence of aluminum chloride are capable of condensing with either benzene [1] or thiophene [2] to give the corresponding ω-benzoylalkylcarboxylic acids (yields 33-77%) or ω-(2-thenoyl)alkylcarboxylic acids (yields 56-96%). The possibility of obtaining keto acids of the selenophene series by such a procedure was established on the example of synthesizing β-(2-selenoyl)propionic acid [3].

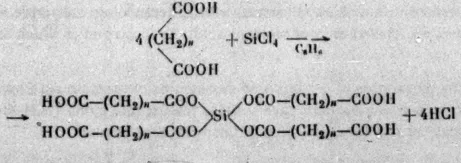
However, in these papers the question of the structure of the silicoanhydrides of dibasic acids was left open. Based on general considerations, the structure of the silicoanhydride of a dibasic acid, formed under the indicated conditions, may be depicted by the following structural formulas.



(I)

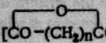


(II)



(III)

With respect to the experimental data obtained by us in the acylation of benzene and thiophene with the silicoanhydrides of saturated dibasic organic acids, it should be mentioned that the only reaction products obtained here were the keto acids, and not in a single case did we observe the secondary formation of diketones – symmetrical dibenzoyl- and di(2-thenoyl)-alkanes.

In contrast to this is the fact that, together with keto acids, diketones are always formed when the benzene ring is acylated with the carboxylic anhydrides of dibasic acids. Thus, the condensation of glutaric anhydrides with benzene in the presence of anhydrous aluminum chloride gives both γ-benzoylbutyric acid (24%) and α,γ-dibenzoylpropane (18.5%) [4]. For the condensation to go in the two indicated directions is even more characteristic for the anhydrides of the higher dibasic acids: when benzene was acylated with the polymeric anhydrides of adipic and sebacic acids  $[\overbrace{CO-(CH_2)_nCO}^{O}]_x$, besides the corresponding ω-benzoyl aliphatic acids, the corresponding diketones and dibasic acids were formed in a ratio that corresponded to the equation proposed by Hill [5], and, respectively, x/2 : x/4 : x/4.

In a similar manner, the acylation of thiophene with the polymeric anhydrides of the higher dibasic acids in the presence of anhydrous stannic chloride gave a mixture of reaction products, composed of the corresponding keto acid, diketone and dibasic acid [6].

The acylation of benzene with the acid chlorides of dibasic acids gives both keto acids and diketones, in which connection some of the keto acids are obtained only if the reactants are taken in a 1 : 1 molar ratio [7, 8]. When the reactants are taken in the ratio of 2 moles of benzene to 1 mole of acid chloride, the reaction goes entirely in the direction of forming the diketone.

The absence of diketones in the products of the acylation of benzene and thiophene with the silicoanhydrides of dibasic acids served as important, but not conclusive, evidence that these silicoanhydrides, formed in the medium of a neutral solvent, have the structure of (III). Since one-half as much hydrogen chloride should be liberated in the formation of structure (III) as in the formation of either structure (I) or (II) (based on the amount of dibasic acid taken for reaction), then, to answer the question as to the structure of the silicoanhydrides of dibasic acids, we ran a series of experiments on the preparation of silicosuccinic anhydride, in which the amount of hydrogen chloride liberated was determined.

The obtained results served as convincing evidence that structure (III) is valid: the amount of hydrogen chloride, liberated in the reaction of silicon tetrachloride with succinic acid in absolute-benzene medium, corresponded to the formation of this structure.

The analysis results obtained for the formed silicosuccinic anhydride also speak in favor of structure (III): its average silicon content was 5.36% (5.31 and 5.41%), as compared to a theoretical value of 5.65% for structure (III). The calculated amount of silicon for structures (I) and (II) is 10.78%.

A comparison of the experimental data with the calculated, given in the Table, convincingly shows that the silicosuccinic anhydride, formed in the above-described manner from succinic acid and silicon tetrachloride, has the structure of (III), in which the free carboxyl groups in each of the four acid radicals, linked to the silicon atom, are retained.

Consequently, the structure of the silicoanhydrides of saturated dibasic acids is such that when they are used to acylate either the benzene or the thiophene ring under the conditions of the Gustavson–Friedel–Crafts reaction, only the corresponding keto acids are obtained, without the diketones as a by-product. Also, if substantial amounts of other silicoanhydride forms of the dibasic acid with the possible structures of (I) and (II) had been formed, then we would have observed the secondary formation of diketones, which, however, did not occur.

Conclusive proof of the structure of the silicoanhydrides of dibasic organic acids would also be the preparation of the acid esters of dibasic acids from them when reacted with an alcohol, or of the substituted monoamides of dibasic acids when reacted with amines. However, when silicosuccinic anhydride was reacted with anhydrous ethyl alcohol we obtained the diethyl ester of succinic acid, the formation of which is obviously associated with secondary processes.

Experiments on the preparation of a substituted monoamide of succinic acid by reacting diethylamine with silicosuccinic anhydride in benzene medium gave positive results: the mono-(N,N-diethyl)amide of succinic acid was obtained without the substituted diamide of this acid as by-product.

$$Si(OCOCH_2CH_2COOH)_4 + 4(C_2H_5)_2NH \rightarrow 4(C_2H_5)_2NCOCH_2CH_2COOH + Si(OH)_4$$

Consequently, the structure of the silicoanhydrides of dibasic acids is actually expressed by the (III) structure proposed by us.

EXPERIMENTAL

Preparation of silicosuccinic anhydride. The experiments were run in a three-necked flask (750 ml), fitted with a stirrer and an efficient reflux condenser, the latter closed with a stopper fitted with an outlet tube, connected to a wash bottle filled with anhydrous kerosene. The wash bottle was connected to two absorption flasks containing standard sodium hydroxide solution. A tube, descending to the bottom of the flask, was also inserted in the reaction flask, and a stream of dry air was passed through it in order to displace the reaction hydrogen chloride.

Expt. No.	Taken for reaction				Amount				Si (in %)		
	succinic acid		silicon tetra-chloride		of hydrogen chloride (in g)		of sodium hydroxide, required to neutralize the hydrogen chloride (in g)		found	calculated for the formula of structure	
	in g	in g-mole	in g	in g-mole	found	calc.*	found	calc.*		(I) and (II) $C_8H_8O_8Si$	(III) $C_{16}H_{20}C_{16}Si$
1	5.9	0.05	4.25	0.025	2.09**	1.82	2.3**	2.0	–	–	–
2	5.9	0.05	2.12	0.0125	1.57	1.82	1.73	2.0	–	–	–
3	11.8	0.1	8.5	0.05	3.59	3.65	3.93	4.0	5.31 5.41	10.78	5.65

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*Amount of hydrogen chloride in grams (and the amount of sodium hydroxide equivalent to it) calculated for the silicosuccinic anhydride having the formula of structure (III); these amounts are double for the case of structures (I) and (II).

**The high result is due to the use of too strong an air current, which carried out a small amount of silicon tetrachloride from the wash bottle containing kerosene; evidence of this was the appearance of turbidity in the first absorption flask containing standard sodium hydroxide solution.

Into the flask were charged 0.05-0.1 g-mole of succinic acid, 500 ml of absolute benzene and 0.0125-0.05 g-mole of silicon tetrachloride. The reaction mixture was heated on the water bath with constant stirring, first at 70-80°, and then on the boiling-water bath. The liberated hydrogen chloride was purified from traces of entrained silicon tetrachloride by passing through the wash bottle with kerosene,(in which the $SiCl_4$ is readily soluble) and then it was absorbed in the vessels containing the standard alkali. At the end of experiment (hydrogen chloride was no longer evolved) the contents of the absorption flasks were transferred to a volumetric flask, and the amount of sodium hydroxide consumed for the reaction was determined by titration with hydrochloric acid. The results, obtained in these experiments, are summarized in the Table.

In Expt. 3, on conclusion of reaction, the benzene and excess silicon tetrachloride were vacuum-distilled, and the residue was analyzed for silicon.

It should be emphasized that although a double amount of silicon tetrachloride was taken in Expt. 3, still the amount of hydrogen chloride liberated was approximately the same as that liberated in Expt. 2, where the silicon tetrachloride was taken in an equimolar amount, i.e., in the amount needed to form the silicoanhydride with structure (III).

For comparison we have given in the Table the calculated percent of silicon, which should correspond to each of the three possible formulas for the structure of the silicoanhydride of succinic acid.

Reaction of ethyl alcohol with silicosuccinic anhydride. A benzene solution of silicosuccinic anhydride, obtained as described above from 11.8 g (0.1 mole) of succinic acid and 3.5 ml (0.03 mole) of silicon tetrachloride in 400 ml of benzene, was distilled to remove 200 ml of benzene; then a stream of dry air was passed to remove any hydrogen chloride, after which the solution was cooled to room temperature, 4.6 g (0.1 mole) of anhydrous ethyl alcohol was added, and the whole was stirred for four hours. The silicic acid was filtered, the benzene was vacuum-distilled at 40-50°, and the residue was distilled. We obtained 2 g (26.5%) of diethyl succinate with b.p. 102-105° (14 mm). Literature: b.p. 103° (14 mm) [9].

Mono-(N,N-diethyl)amide of succinic acid. A benzene solution of silicosuccinic anhydride, obtained as described above from 11.8 g (0.1 mole) of succinic acid and 3.5 ml (0.03 mole) of silicon tetrachloride, was treated dropwise with 14.6 g (0.2 mole) of diethylamine, after which the mixture was heated for 5-6 hours on the water bath, first at 50-60°, and then on the boiling-water bath. After cooling, the silicic acid was filtered and washed with hot acetone. The solvents were distilled off and the residue was vacuum-distilled. We obtained 7 g (44.5%) of product with b.p. 160° (7 mm), and m.p. 83-84° (from acetone). Literature: m.p. 82.1-84.1° [10].

Found %: C 55.82, 55.86; H 8.93, 8.99. Equiv. 174.4, 173.7. $C_8H_{15}O_3N$. Calculated %: C 55.49; H 8.73. Equiv. 173.2

SUMMARY

The reaction of a saturated dibasic organic acid with silicon tetrachloride in an inert solvent yields the silicoanhydride of the dibasic acid, in which the silicon atom is linked to four radicals of the dibasic acid with retention of a free carboxyl group in each radical.

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TETRAACYLOXYSILANES IN ORGANIC SYNTHESIS

XIX. SYNTHESIS OF 3- AND 4-NITROCINNAMIC ACIDS AND THEIR HOMOLOGS [α-ALKYL-β-(NITROPHENYL)ACRYLIC ACIDS]

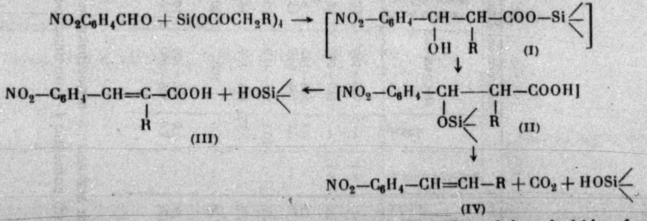
Iu.K. Iur'ev, A.N. Vysokosov and S.N. Godovikova

In previous papers two of us had shown that the mixed anhydrides of saturated monobasic organic acids and orthosilicic acid (tetraacyloxysilanes) will condense with benzaldehyde and other aldehydes of an aromatic character, like furfural and 2-thiophenecarboxaldehyde, to yield the corresponding α,β-unsaturated acids of the benzene [1], furan [2] and thiophene [2] series.

The preparation of cinnamic and 2-furylacrylic acids and their homologs by such a procedure, and also of 2-thienylacrylic acid (in high yields), is convincing evidence that the hydrogen atoms in the α-methylene groups of the silicoanhydrides of organic acids are no less labile than those found in the anhydrides of organic acids. Due to the strong electronegativity of the $\cdot Si(OCOCH_2R)_3$ radical, it is possible that the mobility of the hydrogen atoms in the methylene group of the silicoanhydrides of organic acids, $Si(OCOCH_2R)_4$, is even somewhat greater than in the anhydride of the same acid.

In this paper we condensed the silicoanhydrides of saturated monobasic organic acids with m- and p-nitrobenzaldehyde, and in this way obtained the following nitrocinnamic acids in high yields: 3-nitrocinnamic (83.5%), 4-nitrocinnamic (89.5%), 4-nitro-α-methylcinnamic (88%), 4-nitro-α-ethylcinnamic (87%), 4-nitro-α-propylcinnamic (47%), 4-nitro-α-isopropylcinnamic (59%) and 4-nitro-α-butylcinnamic acid (67.5%).

We used sodium acetate as the condensing agent in the reaction of m- and p-nitrobenzaldehyde with silicoacetic anhydride, and potash in the condensations with the silicoanhydrides of the other acids.



$$NO_2C_6H_4CHO + Si(OCOCH_2R)_4 \longrightarrow [NO_2{-}C_6H_4{-}\underset{OH}{CH}{-}\underset{R}{CH}{-}COO{-}Si\lessdot] \quad (I)$$

$$NO_2{-}C_6H_4{-}CH{=}\underset{R}{C}{-}COOH + HOSi\lessdot \ (III) \longleftarrow [NO_2{-}C_6H_4{-}\underset{OSi\lessdot}{CH}{-}\underset{R}{CH}{-}COOH] \quad (II)$$

$$NO_2{-}C_6H_4{-}CH{=}CH{-}R + CO_2 + HOSi\lessdot \quad (IV)$$

It should be emphasized that a similar behavior of the silicoanhydrides and the anhydrides of organic acids in the Perkin reaction is also manifested in the fact that when the condensation is run with the indicated nitrobenzaldehydes, as well as other nitrobenzaldehydes, the reaction in both cases goes to greater completion and leads to higher yields of the corresponding nitrocinnamic acid than is true for the unsubstituted cinnamic acids.

The stabilizing influence exerted by the nitro group in the carbonyl-containing reaction component is undoubtedly manifested in the intermediate stage of the reaction, where the ester of the orthosilicic and α-alkyl-β-(nitrophenyl)-β-hydroxyhydracrylic acids (II), formed from the addition product (I), loses silicic acid with the formation of the α-alkyl-β-(nitrophenyl)acrylic acid (III) more easily than it suffers decarboxylation and the cleavage of silicic acid with the formation of the nitrostyrene homolog (IV), the secondary product of this process.

In this connection it should be mentioned that when we condensed silicoisovaleric anhydride with p-nitrobenzaldehyde, both under mild conditions – at 100° for 20 hours, and under more drastic conditions – at 165-170°

Reaction components (in g)						Reaction conditions		acid	Reaction products									Literature melting point
silicoanhydride		m-nitrobenzaldehyde	p-nitrobenzaldehyde	sodium acetate	potash	temperature	time of heating (in hours)		yield		constants and analysis data							
name	amount								in g	in %	melting point	% C		% H		% N		
												found	calc.	found	calc.	found	calc.	
Silicoacetic	13.2	3.8	—	4.1	—	180—185°	12	3- Nitrocinnamic	4.0	83.5	200—201°*	—	—	—	—	—	—	200—201° [3]
»	26.4	—	7.55	8.2	—	180—185	12	4- Nitrocinnamic	8.6	89.5	287.5—288**	—	—	—	—	—	—	285—286° [4];
»	13.2	—	7.55	—	6.9	180—185	8	»	4.0	41.5	287.5—288**	—	—	—	—	—	—	287° [5]; 288° [3, 6]
Silicopropionic	12.0	—	3.78	—	5.2	165—170	15	4- Nitro-α-methylcinnamic	4.6	88.0	207.5—208	58.07, 58.02	57.97	4.45, 4.40	4.38	6.52, 6.67	6.76	208° [7, 8]
Silicobutyric	28.2	—	7.55	—	10.4	165—170	15	4- Nitro-α-ethylcinnamic	9.6	87.0	169—169.5	59.75, 59.89	59.71	5.07, 5.13	5.01	6.42, 6.39	6.33	168—169° [9]
Silicovaleric	11.0	—	3.78	—	3.75	165—170	15	4- Nitro-α-propylcinnamic	2.85	47.0	134—134.5	61.26, 61.21	61.27	5.51, 5.48	5.57	6.10, 6.17	5.96	132—134° [9]
Silicoisovaleric	22.0	—	7.56	—	7.0	100	20	4- Nitro-α-isopropylcinnamic	6.9	59.0	178—179	61.19, 61.22	61.27	5.58, 5.50	5.57	6.08, 6.13	5.96	Not described in the literature
»	22.0	—	7.56	—	7.0	165—170	10	»	4.2	36.0	178—179	—	—	—	—	—	—	Ditto
Silicocaproic	24.4	—	3.78	—	7.0	165—170	10	4- Nitro-α-butylcinnamic	4.2	67.5	162.5—163	62.21, 62.30	62.23	6.16, 6.20	6.18	5.39, 5.38	5.62	162—163° [9]

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*The mixed melting point with authentic 3-nitrocinnamic acid was not depressed.

**The mixed melting point with authentic 4-nitrocinnamic acid was not depressed.

for 10 hours, we obtained 4-nitro-α-isopropylcinnamic acid in a yield of 59% and 36%, respectively. When we condensed the silicoisovaleric anhydride with benzaldehyde [1] the principal and solitary reaction product obtained by us was 1-phenyl-3-methyl-1-butene (α-phenyl-β-isopropylethylene) (70% yield).

EXPERIMENTAL

The tetraacyloxysilanes used in the present study were obtained by the earlier-described procedure [1].

A mixture of 0.05-0.025 g-mole of p-nitrobenzaldehyde, 0.05-0.025 g-mole of the silicoanhydride of the organic acid and 0.05-0.025 g-mole of either anhydrous sodium acetate or potash, contained in a 100-ml flask fitted with an air reflux condenser (connected to a calcium chloride tube) and stirrer, was heated in an oil bath (with thermometer) with good stirring.

The mixture after cooling was treated with 2 N sodium hydroxide solution until faintly alkaline (to litmus) [1], then diluted with water to a volume of 300-400 ml, heated to 80°, and filtered. The filtrate was acidified with concentrated hydrochloric acid (to litmus), then allowed to stand in the cold for 2-3 hours, and the nitrocinnamic acid separated and recrystallized from alcohol.

The results obtained by us are summarized in the Table.

SUMMARY

The condensation of the silicoanhydrides of saturated monobasic organic acids with m- and p-nitrobenzaldehyde in the presence of either sodium acetate or potash permits obtaining the corresponding nitrocinnamic acids in high yields, even in the case where the silicoanhydride is formed from an acid with a branched radical.

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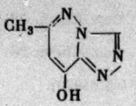
REACTIONS OF HYDRAZINE DERIVATIVES

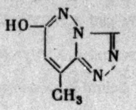
XIX. CONDENSATION OF 4-AMINO-[1,2,4]-TRIAZOLE WITH ESTERS

A.N. Kost and F. Gents

The heating of hydrazine with formic acid readily yields 4-amino-[1,2,4]-triazole [1]. Despite the presence of four nitrogen atoms, this amine is more acidic than basic [2]; however, the amino group in this compound is still capable of entering into various condensation reactions, at times, with simultaneous involvement of the hydrogen atoms in the triazole ring (in positions 3 and 5). Thus, for example, even Bülow [3] showed that when the aminotriazole is heated with acetylacetone it suffers condensation, with the cleavage of water and the formation of 6,8-dimethyl-[1,2,4]-triazolo-(b)-pyridazine (I).* The reaction with acetoacetic ester goes in a similar manner, in which connection a compound is formed to which Bülow [5] has assigned the structure (IIa); in our opinion the compound has the more probable structure of 6-hydroxy-8-methyl-[1,2,4]-triazolo-(b)-pyridazine (IIb).



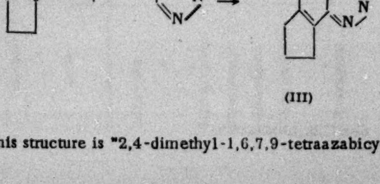
(IIa)



(IIb)

Methylacetoacetic and benzoylacetic esters react in a similar manner with the aminotriazole [6]. It should be mentioned that the reaction goes even at the boil when run in either alcohol or acetic acid solution, i.e., it goes with much greater ease than in the case, for example, of the condensation of aniline with acetoacetic ester to give 4-hydroxyquinaldine [7].

In view of the fact that hydroxytriazolopyridazines are capable of forming complexes with metal cations [5, 6], we became interested in them and synthesized a number of their class. For this the proper β-keto ester was mixed with the 4-aminotriazole and the mixture heated for 20-30 minutes at 180-200° (the reaction alcohol and water are removed by distillation). If the reaction was too vigorous, as, for example, was true in the case of 2-carbethoxycyclopentanone (with the formation of compound III), then xylene, toluene or benzene was added to the reactant mixture and the reaction alcohol and water slowly removed by azeotropic distillation. At times we added the hydrochloride of the aminotriazole to serve as condensing agent. It is interesting to mention that the yield depended greatly on the rate of heating. If the temperature was raised slowly, then much tar formation occurred.



(III)

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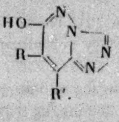
*The systematic name [4] for this structure is "2,4-dimethyl-1,6,7,9-tetraazabicyclo-[5–9]-nonatetraene."

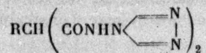
In the case of 2-carbethoxycyclohexanone we were unable to obtain a condensation product even under the mildest conditions. The reaction goes with much tar formation, in which connection water is the main cleavage product. It is possible that this is due to the large degree of enolization shown by the keto ester, since, according to Dieckmann [8], 2-carbethoxycyclopentanone contains 4% of the enol form, while in the case of 2-carbethoxycyclohexanone the content of the enol form reaches 76%. In support of this theory is the fact that succinylsuccinic ester, which is almost completely enolized [9], cleaves water even more easily, reacting with the aminotriazole apparently through the enolic hydroxyl. Tar formation is also very readily incurred when cleavage of the alcohol is attempted, either by direct heating (0.5 hour at 160-170°) or by refluxing in acetic acid. Such a result was obtained when we attempted to condense the aminotriazole with α-formylphenylacetic ester (2 hours, 170°). We were also unable to extend the reaction to γ-keto esters: only tar formation was observed when the aminotriazole was heated with the ethyl ester of cyclopentanone-2-acetic acid [10] for 25 minutes at 190-210°. The same thing occurred when the water was removed from the reactant mixture by azeotropic distillation with toluene.



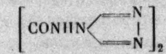
(IV) R = C_2H_5, R' = CH_3
(V) R = C_4H_9-n., R' = CH_3
(VI) R = $C_6H_5CH_2$, R' = CH_3
(VII) R = C_4H_9-n., R' = C_5H_{11}-n.
(VIII) R = H, R' = C_2H_5
(IX) R = C_6H_5, R' = $C_6H_5CH_2$

Having obtained compounds (I-IX) in the indicated manner, we next condensed the aminotriazole with malonic ester, assuming that similar to aniline, which gives dihydroxyquinoline with malonic ester, the aminotriazole would form the dihydroxytriazolopyridazine. However, it proved that the malonic ester, even when taken in large excess, reacts (when heated) with two molecules of the aminotriazole, forming N,N'-bis-(1,2,4-triazol-4-yl)-malonamide (X). Cyclization products involving the hydrogen atoms of the triazole ring could not be found. The structure of diamine (X) was shown by its infrared absorption spectrum,* which revealed the presence of maxima at 1690 (corresponds to the C—O bond) and 3084 cm^{-1} (corresponds to the C—N bond in the amido group). An acetic acid solution of this amide in the presence of sodium acetate precipitates the ions Cu^{2+}, Ni^{2+} and Co^{2+} from water solution, but does not precipitate Al^{3+}, Cd^{2+}, Bi^{3+} and Th^{4+}. Not one of these cations is precipitated in alkaline medium (in the presence of tartrate buffer).

The reaction does not go as well with ethylmalonic ester, and here we obtained the N,N'-bis-(1,2,4-triazol-4-yl)-amide of ethylmalonic acid (XI) in a yield of only 15.2%. In the case of butylmalonic ester only traces of a compound with m.p. 255-258° was isolated, while in the case of the diethyl ester of diethylmalonic acid we were unable to make the condensation go even after heating for 20 hours at 190-200°.



R = H (X), C_2H_5 (XI).



(XII)

When the aminotriazole is reacted with diethyl oxalate it could be expected that the bicyclic compound would also be formed, but instead we obtained N,N'-bis-(1,2,4-triazol-4-yl)-oxamide (XII) in 54.1% yield. The infrared spectrum of this compound (maxima at 1698 and 3110 cm^{-1}) is similar to that of malonamide (X). A compound with m.p. 162-163.5° was isolated as a secondary product, but its structure was not determined.

Recently a paper was published in which it was stated that the oxalyldihydrazone of cyclohexanone is an extremely sensitive reagent for Cu^{2+} ions [11]. Based on a structural analogy, our diamide (XII) also precipitates Cu^{2+}, Mg^{2+} and Cd^{2+} ions in alkaline media containing tartrate buffer, and Cu^{2+} ions in a medium containing acetate buffer, but it does not precipitate Al^{3+} and Fe^{3+} ions. We propose to make a more detailed study of this compound as a test reagent for metal cations.

Continuing our study of the ability shown by the aminotriazole to condense, we found that under the usual conditions (boiling in the presence of either alkaline or acidic agents) it fails to react with methyl methacrylate, but with acrylonitrile, which is much more reactive, in the presence of alkali, it quite readily gives the dicyanoethylation product (XIII). In acid media or without catalysts the reaction does not go. It should be mentioned that up to now the cyanoethylation of amines, the NH_2 group of which is linked to a heterocyclic ring, has been unsuccessful [12]. In the present case the amino group functions not as an amine, but as an amide.

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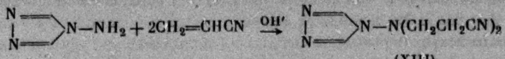
*The spectra were taken by B.V. Lokshin using an IKS-11 spectrophotometer (LiF prism).


(XIII)

From the above-presented material it is obvious that under ordinary conditions the carbethoxy group acylates only the amino group of the aminotriazole, with practically no involvement of the hydrogen atoms in the ring. This makes it possible to state that the condensation of β-keto esters with the aminotriazole goes in such manner that the carbethoxy group also acylates the amino group, while the keto group cleaves the elements of water with involvement of the hydrogen atom in the 3 position of the triazole ring. Expressed differently, the reaction product has the structure of the 6-hydroxy-, and not of the 8-hydroxy-triazolopyridazine (corresponding to IIb, and not to IIa). We propose to obtain a more accurate answer to this problem through countersyntheses.

Bülow indicated that the triazolopyridazines are powerful poisons [3]. For this reason we sent a number of the compounds synthesized by us to the Department of Vertebrate Zoology at Moscow University, where the tests were run by N.M. Dukel'skaia. It was found that compounds (I, VI, X, XII and XIII), when administered "per os" (with food) to rats in three consecutive doses (in portions of 170-180 mg/kg of body weight), showed very little toxic effect. When administered intravenously to rabbits in a dose of 200 mg/kg it proved that compound (XIII) was toxic (breathing paralyzed), while compound (XII) in the same dosage was not poisonous. Consequently, the toxicity of the indicated compounds was slight.

EXPERIMENTAL

4-Amino-[1,2,4]-triazole. Into a two-liter flask, fitted with a reflux condenser and cooled externally with a stream of water, was charged 540 g of 85% formic acid, and then gradually (in 40 minutes), with occasional shaking, 780 g of 96% hydrazine hydrate was added. When brisk reaction had subsided the reflux condenser was replaced by a descending one, and the water and excess hydrazine were removed by distillation. The distillation began at a mixture temperature of 115°, and in five hours the temperature reached 200°. The mixture was kept at this temperature for four hours, then it was cooled, and a mixture of 750 ml of alcohol and 750 ml of ether was added. On standing in the refrigerator at −10°, the solution deposited white crystals of 4-amino-[1,2,4]-triazole, which were filtered, washed with ether, and dried in a vacuum-oven. We obtained 318 g (75.7%) of substance with m.p. 79-80° [1]. If the amount of reactants is reduced to 1/10 of that above, then the yield rises to 93-95%.

The dimethyltriazolopyridazine (I) was obtained when the aminotriazole was heated with acetylacetone [3]. In a similar manner, using the Bülow method [5], we synthesized the 6-hydroxy-8-methyltriazolopyridazine (II) from the aminotriazole and acetoacetic esters.

6-Hydroxy-8-methyl-7-ethyl-[1,2,4]-triazolo-(b)-pyridazine (IV). Into a round-bottomed flask, fitted with a thermometer that reached the reaction mixture, was charged 2.1 g of the 4-aminotriazole and 4 g of ethylacetoacetic ester with b.p. 75-78° (7 mm) and n_D^{20} 1.4212. The mixture was heated in a metal bath at 170°. A brisk boiling of the reaction mass began at this temperature and the water and alcohol began to distill. The mixture was kept at 170-190° for 30 minutes, then cooled, and finally dissolved in hot water. The crystals that deposited on cooling were filtered, washed with cold water, then with alcohol, and finally dried in a vacuum-oven. We obtained 1.2 g (27%) of 6-hydroxy-8-methyl-7-ethyl-[1,2,4]-triazolo-(b)-pyridazine. After four recrystallizations from 50% aqueous alcohol, m.p. 229-231° (decomp.).

Found %: C 54.12, 53.90; H 5.93, 5.86. $C_8H_{10}ON_4$. Calculated %: C 53.91; H 5.66.

6-Hydroxy-8-methyl-7-butyl-[1,2,4]-triazolo-(b)-pyridazine (V). A mixture of 4.2 g of the 4-aminotriazole and 10 g of butylacetoacetic ester with b.p. 107-108° (12 mm) and n_D^{20} 1.4270 was heated at 190-205° for 30 minutes. The crystalline mass obtained on cooling was dissolved in hot acetic acid, and the deposited crystals of 6-hydroxy-8-methyl-7-butyl-[1,2,4]-triazolo-(b)-pyridazine were filtered and air-dried. Yield 6.1 g (59.2%). After two recrystallizations from 75% acetic acid, m.p. 206°.

Found %: N 27.08, 27.46. $C_{10}H_{14}ON_4$. Calculated %: N 27.17.

6-Hydroxy-8-methyl-7-benzyl-[1,2,4]-triazolo-(b)-pyridazine (VI). A mixture of 8 g of the 4-aminotriazole and 21.2 g of benzylacetoacetic ester with b.p. 116-117° (1 mm) and n_D^{20} 1.4983 was heated rapidly to 180°. In seven minutes at 180-190° the mixture became homogeneous (the alcohol and water had distilled); then the temperature was raised to 190-200°, and in ten minutes the reaction mass swelled up and crystallized. The flask contents were dissolved in hot glacial acetic acid, and after the usual technique of cooling, filtering, washing and drying in a vacuum-oven we obtained 9.2 g (40%) of 6-hydroxy-8-methyl-7-benzyl-[1,2,4]-triazolo-(b)-pyridazine. After two recrystallizations from glacial acetic acid, m.p. 212° (decomp.).

Found %: C 64.87, 65.05; H 5.20, 5.28. $C_{13}H_{12}ON_4$. Calculated %: C 64.97; H 5.04.

6-Hydroxy-7-butyl-8-amyl-[1,2,4]-triazolo-(b)-pyridazine (VII). The Claisen condensation of 0.2 mole of methyl caproate with 0.1 mole of sodium methylate gave 9.7 g (42.5%) of methyl caproylcaproate, b.p. 122-123° (2 mm), n_D^{20} 1.4335. One gram of the 4-aminotriazole and a few crystals of the 4-aminotriazole hydrochloride were added to 3 g of this ester. The mixture was heated at 185-195° for 30 minutes; the crystals obtained on cooling were dissolved in hot alcohol, precipitated by the addition of water, washed with alcohol, then with water, and finally dried in a vacuum-oven. We obtained 0.6 g (18.3%) of 6-hydroxy-7-butyl-8-amyl-[1,2,4]-triazolo-(b)-pyridazine. After four recrystallizations from 50% aqueous alcohol, m.p. 169.5-170.5°.

Found %: C 63.71, 63.95; H 8.66, 8.70. $C_{14}H_{22}ON_4$. Calculated %: C 64.09; H 8.46.

6-Hydroxy-8-ethyl-[1,2,4]-triazolo-(b)-pyridazine (VIII). A solution of 80 g of freshly distilled malonic ester in 50 ml of anhydrous ethanol was added to a suspension of 12.5 g of magnesium in 50 ml of anhydrous ethanol and 0.5 ml of carbon tetrachloride. The mixture was heated cautiously on the water bath until hydrogen began to evolve. When the reaction had subsided somewhat, 150 ml of dry ether was added, and the mixture was heated under reflux until all of the magnesium had dissolved (about seven hours). The solution was cooled and then a solution of 49 g of propionyl chloride in 50 ml of anhydrous ether was added gradually, after which the mixture was heated under reflux for another hour. The mixture after cooling was decomposed with 350 ml of 2 N sulfuric acid, then with water, dried over magnesium sulfate, and the ether removed by vacuum-distillation. The residue was treated with 8 g of β-naphthalenesulfonic acid monohydrate, and then the mixture was slowly heated under air reflux to 200° (gas began to evolve at 130°). After heating for five hours the gas evolution ceased, and the mixture was cooled, diluted with ether, washed three times with soda solution, then twice with water, and the water extracts extracted with ether. The combined ether extracts were dried over magnesium sulfate, the ether was distilled off, and the residue was vacuum-distilled. We obtained 20.6 g (34.5%) of the propionylacetate, b.p. 67-72° (5 mm), n_D^{20} 1.4230 [13].

A mixture of 2.1 g of the 4-aminotriazole and 4.3 g of the above keto ester was heated for 1.5 hours at 160-170°. The crystals obtained on cooling were dissolved in hot glacial acetic acid and then reprecipitated by the addition of water. After filtration, washing with water and drying in the air we isolated 1.6 g (39%) of 6-hydroxy-8-ethyl-[1,2,4]-triazolo-(b)-pyridazine. After two recrystallizations from 30% acetic acid, m.p. 236.5-237.5°.

Found %: C 51.17, 51.37; H 5.09, 5.10. $C_7H_8ON_4$. Calculated %: C 51.21; H 4.91.

6-Hydroxy-7-phenyl-8-benzyl-[1,2,4]-triazolo-(b)-pyridazine (IX). Ethyl phenylacetate (0.15 mole) was added gradually, with cooling, to an ether solution of 0.25 mole of isopropylmagnesium bromide. When gas (propane) evolution had ceased the mixture was allowed to stand at room temperature for two hours, then 200 ml of ether was added, and the mixture decomposed with 2 N sulfuric acid and ice. The ether layer was washed with water, then with sodium bicarbonate solution, again with water, and finally it was dried over magnesium sulfate. Most of the ether was evaporated, and the resulting crystals were filtered, washed with alcohol, and air-dried. We obtained 13.5 g (61.5%) of the α,γ-diphenylacetoacetic ester with m.p. 77-78° [14].

A solution of 4 g of the above ester and 1 g of the 4-aminotriazole in 20 ml of glacial acetic acid was heated under reflux for 46 hours. Then the acetic acid was removed by vacuum-evaporation on the water bath, and the residual oil was treated with water. Colorless crystals separated after standing for a day, which were filtered, washed with ether, and vacuum-dried. We obtained 0.3 g (8.3%) of 6-hydroxy-7-phenyl-8-benzyl-[1,2,4]-triazolo-(b)-pyridazine. After recrystallization from 70% acetic acid, m.p. 286-290°. An attempt to run the reaction at 180-200° (0.5 hour) without solvent led to pronounced tarring.

Found %: C 71.59, 71.66; H 4.78, 4.83. $C_{18}H_{14}ON_4$. Calculated %: C 71.51; H 4.67.

6-Hydroxy-7,8-trimethylene-[1,2,4]-triazolo-(b)-pyridazine (III). Into a Wurtz flask was charged 2.1 g of the 4-aminotriazole, 4.7 g of 2-carbethoxycyclopentanone and 60 ml of dry xylene. The mixture was heated slowly, the reaction alcohol and water being removed by azeotropic distillation with the xylene. When about 10 ml of liquid remained in the flask, it was treated with another 60 ml of xylene, and the distillation repeated. The dark residue, which crystallized on cooling, was dissolved in glacial acetic acid, the crystals reprecipitated by the addition of water, after which they were filtered, washed with alcohol, then with water, and finally vacuum-dried. We obtained 1.95 g (45.4%) of substance (III), which was purified by recrystallization from water with the addition of activated carbon. The colorless crystals obtained in this manner decomposed when heated above 250° and melted with strong decomposition at 292-295°.

Found %: C 54.35, 54.50; H 4.82, 4.95. $C_8H_8ON_4$. Calculated %: C 54.54; H 4.57.

N,N'-Bis-(1,2,4-triazol-4-yl)-malonamide (X). A mixture of 8.4 g of the 4-aminotriazole and 50 ml of malonic ester was heated in a Wurtz flask immersed in an oil bath. Frothing and the distillation of alcohol began at 170°. In 20 minutes at 170-180° the whole mass solidified. It was cooled, and the crystals after washing with alcohol and ether were dried in a vacuum-desiccator over phosphorus pentoxide. We obtained 7.2 g (61%) of diamide (X). After two recrystallizations from water, m.p. 265-270° (decomp.).

Found %: N 47.11, 47.38. $C_7H_8O_2N_8$. Calculated %: N 47.46.

N,N'-Bis-(1,2,4-triazol-4-yl)-amide of ethylmalonic acid (XI). A mixture of 16 ml of ethylmalonic ester and 4.2 g of the 4-aminotriazole was heated at 190-200° for 30 minutes. The mixture after cooling was treated with 30 ml of acetone, and after a day the crystals were separated by filtration, washed with water, and vacuum-dried. We obtained 1.0 g (15.2%) of diamide (XI), which after recrystallization from a mixture of anhydrous ethanol and glacial acetic acid (3 : 1), and then from 50% ethanol, had m.p. 247-248° (decomp.).

Found %: N 42.11, 42.10. $C_9H_{12}O_2N_8$. Calculated %: N 42.41.

N,N'-Bis-(1,2,4-triazol-4-yl)-oxamide (XII). A mixture of 17 g of the 4-aminotriazole and 58.4 g of diethyl oxalate was heated at 150-170° for 40 minutes, then cooled, treated with hot alcohol, and the crystals separated. After washing with alcohol, then with water and drying in a vacuum-oven we obtained 12 g (54.1%) of diamide (XII). The substance was purified by repeated precipitation from aqueous alkaline solution with acetic acid. The pure compound did not melt up to 360°, is soluble in chloroform, ether, benzene and dioxane, is very difficultly soluble in alcohol, water and glacial acetic acid, and is readily soluble in dilute aqueous alkali solutions.

Found %: N 50.41, 50.86. $C_6H_6O_2N_8$. Calculated %: N 50.44.

The alcohol solution on cooling deposited 0.4 g of yellowish needle crystals. After recrystallization from alcohol, m.p. 162-163.5°. Found %: C 45.46, 45.47; H 5.83, 5.87. The Lassaigne test for nitrogen was positive. The substance is readily soluble in water and in hot alcohol, and is insoluble in ether. Its structure was not investigated in greater detail.

4-(Di-β-cyanoethyl)-amino-[1,2,4]-triazole (XIII). Acrylonitrile (5.3 g) was added dropwise at room temperature to a solution of 8.4 g of the 4-aminotriazole and 0.1 g of sodium hydroxide in 200 ml of tert-butyl alcohol. Heat was evolved and the mixture turned red, after which crystals began to form. The reaction mass was heated for ten minutes on the water bath, and the crystals obtained on cooling were separated, washed with alcohol, and vacuum-dried. We obtained 7.1 g (74.8%) of dinitrile (XIII). After two recrystallizations from a mixture of alcohol and ether (3 : 1), m.p. 168-169°. The substance is readily soluble in water and hot alcohol, difficultly soluble in benzene, and very difficultly soluble in petroleum ether and chloroform.

Found %: C 50.63, 50.78; H 5.33, 5.68. $C_8H_{10}N_6$. Calculated %: C 50.51; H 5.30.

SUMMARY

1. We synthesized a number of 6-hydroxy-[1,2,4]-triazolo-(b)-pyridazines by the condensation of 4-amino-[1,2,4]-triazole with β-keto esters.

2. It was shown that diethyl oxalate and malonic ester do not react with the aminotriazole to give bicyclic compounds of the dihydroxytriazolopyridazine type, but instead give the corresponding ditriazolyldiamides.

3. The cyanoethylation of 4-aminotriazole, proceeding in alkaline medium, was described.

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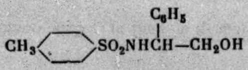
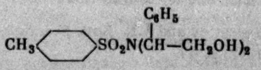
REACTION OF ARYLSULFONAMIDES WITH PROPYLENE OXIDE

A.E. Kretov and E.A. Abrazhanova

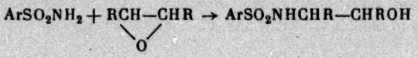
Ethylene oxide has found wide use as a raw material for the preparation of a multitude of products, used as solvents [1], plasticizers [2], lacquers [3], and in the production of explosives, poisons and medicinals [4].

The purpose of the present investigation was to study the reaction of propylene oxide with arylsulfonamides. This reaction is mentioned in the literature in a paper by Johnson [5], who reacted styrene oxide with p-toluenesulfonamide and isolated two products:

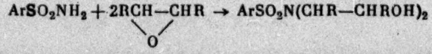




The reaction was studied by us for the case of propylene oxide and the three arylsulfonamides: benzenesulfonamide, p-chlorobenzenesulfonamide and p-toluenesulfonamide. Based on the general reaction scheme for the addition of olefin oxides to the NH_2 group, and the structure of the products isolated by Johnson, it is possible to postulate that the reaction goes in two stages. Consequently, depending on the reaction conditions, it is possible to obtain either mono- or disubstituted arylsulfonamides.



$$ArSO_2NH_2 + RCH{-}CHR\ (\text{O}) \rightarrow ArSO_2NHCHR{-}CHROH \qquad (1)$$



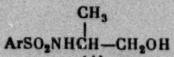
$$ArSO_2NH_2 + 2RCH{-}CHR\ (\text{O}) \rightarrow ArSO_2N(CHR{-}CHROH)_2 \qquad (2)$$

We ran the reaction in an autoclave at a pressure of 15-25 atm in the presence of sodium hydroxide as catalyst. It proved that in the case of benzenesulfonamide the main reaction product under these conditions is N-(β-hydroxyisopropyl)benzenesulfonamide (I). In the case of p-toluenesulfonamide and p-chlorobenzenesulfonamide, the reaction goes according to schemes 1 and 2 with the formation of the corresponding substituted amides.

From the literature it is known that certain products, similar to those obtained by us, were synthesized by the condensation of the sodium derivative of p-toluenesulfonamide with ethylene chlorohydrin [6].

The N-(β-hydroxyisopropyl)arylsulfonamides (A) are sirupy, noncrystallizing liquids that cannot be vacuum-distilled without decomposition, and are soluble in aqueous alkali solutions, benzene, ether and alcohol. They were purified by conversion to the corresponding sodium derivatives, which were obtained as crystalline compounds with several molecules of crystallization water, and proved to be insoluble in organic solvents. The crystallization water was lost when the compounds were heated in vacuo at 120-130°.

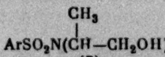
The N-(β,β'-dihydroxydiisopropyl)arylsulfonamides (B) are colorless crystalline compounds, insoluble in alkalies, and soluble in hot carbon tetrachloride and petroleum ether.



$$ArSO_2NH\overset{CH_3}{\overset{|}{C}}H{-}CH_2OH$$

(A)

(I) $Ar = C_6H_5$,
(II) $Ar = C_6H_4CH_3$-p,
(III) $Ar = C_6H_4Cl$-p,

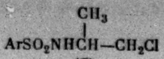


$$ArSO_2N(\overset{CH_3}{\overset{|}{C}}H{-}CH_2OH)_2$$

(B)

(IV) $Ar = C_6H_4CH_3$-p,
(V) $Ar = C_6H_4Cl$-p.

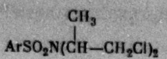
To confirm the structure of the obtained compounds we studied some of their chemical properties. The products obtained by the halogenation and acylation of the hydroxyl group were synthesized. We used thionyl chloride and phosphorus pentachloride to replace the hydroxyl group by chlorine. Here we obtained colorless crystalline products (C) and (D), which could be titrated with aqueous alkali solutions, and were soluble in ether, benzene, alcohol, hot petroleum ether and carbon tetrachloride.



$\mathrm{ArSO_2NH\overset{CH_3}{\overset{|}{C}}H{-}CH_2Cl}$

(C)

(VI) Ar = C_6H_5.



$\mathrm{ArSO_2N(\overset{CH_3}{\overset{|}{C}}H{-}CH_2Cl)_2}$

(D)

(VII) Ar = $C_6H_4CH_3$-p,
(VIII) Ar = C_6H_4Cl-p.

For the acylation we used acetyl chloride. Only the N-(β-hydroxyisopropyl)benzenesulfonamide was acylated. The acylation product isolated from the reaction was a sirup, which could not be vacuum-distilled, and titrated as one equivalent in the presence of phenolphthalein.

EXPERIMENTAL

Reaction of propylene oxide with arylsulfonamides. A mixture of the arylsulfonamides (benzenesulfonamide 31.4 g, p-toluenesulfonamide 34.8 g, p-chlorobenzenesulfonamide 38.3 g), 17.4 g of propylene oxide, 0.1 g of NaOH and 200 ml of benzene was heated in an autoclave with stirrer for two hours. A temperature of 200-220° and a pressure of 20 atm was used for the benzenesulfonamide, 240-260° and 25 atm for the p-toluenesulfonamide, and 160-180° and 15 atm for the p-chlorobenzenesulfonamide. The reaction mixture was unloaded from the autoclave after cooling (in 15-20 hours). In the case of benzenesulfonamide, the benzene was vacuum-distilled from the reaction mixture, and the residue dissolved in 10% caustic solution and precipitated by acidification with concentrated hydrochloric acid. The obtained oil was separated, washed with water, and then dissolved in benzene. The benzene solution was dried over sodium sulfate and the benzene was removed by vacuum-distillation. In the case of p-toluenesulfonamide and p-chlorobenzenesulfonamide, a crystalline precipitate deposited from the reaction mixture, which was separated and treated with hot 10% caustic solution. The insoluble portion was recrystallized from either water or carbon tetrachloride. The mother liquor was worked up in the same manner as described above for benzenesulfonamide. In this manner we obtained:

N-(β-hydroxyisopropyl)benzenesulfonamide (I) in 58% yield, N-(β-hydroxyisopropyl)-p-toluenesulfonamide (II) in 15% yield, N-(β-hydroxyisopropyl)-p-chlorobenzenesulfonamide (III) in 5% yield, and N-(β,β'-dihydroxydiisopropyl)-p-toluenesulfonamide (IV) in 60% yield.

M.p. 126-128° (from water), colorless crystals.

Analysis of (IV).

Found %: N 4.45, 4.88. $C_{13}H_{21}O_4NS$. Calculated %: N 4.85.

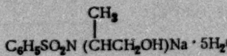
N-(β,β'-Dihydroxydiisopropyl)-p-chlorobenzenesulfonamide (V), yield 48.2%, m.p. 107-110° (from carbon tetrachloride).

Found %: N 4.77. $C_{12}H_{18}O_4NClS$. Calculated %: N 4.56.

The reaction of p-toluenesulfonamide with propylene oxide can be made to go with a predominant formation of the monosubstituted derivative. For this a mixture of propylene oxide and benzene (1 : 1) is used as the solvent and the catalyst is omitted. The reaction mixture is worked up the same as described above. The yield of N-(β-hydroxyisopropyl)-p-toluenesulfonamide (II) in this case was 51%.

Preparation of sodium derivatives of N-(β-hydroxyisopropyl)-arylsulfonamides. To obtain the same derivatives, 5 ml portions of 10% sodium hydroxide solution were added in the cold to 0.01 mole of compounds (I)-(III). The obtained precipitates were filtered and washed with benzene.

Sodium derivative of (I), m.p. 54-56°.

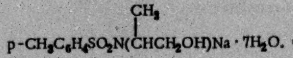


Found %: S 9.72. $\mathrm{C_6H_5SO_2N(\overset{CH_3}{\overset{|}{C}}HCH_2OH)Na\cdot 5H_2O}$. Calculated %: S 9.78.

After heating in vacuo at 120-130°.

Found % N 6.52. $C_9H_{12}O_3NSNa$. Calculated % N 5.92.

Sodium derivative of (II), m.p. 64-66°.

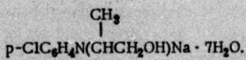


Found % S 8.56. $p\text{-}CH_3C_6H_4SO_2N(\overset{CH_3}{\overset{|}{C}}HCH_2OH)Na \cdot 7H_2O$. Calculated % S 8.50.

After heating in vacuo at 120-135°.

Found % N 6.03. $C_{10}H_{14}O_3NSNa$. Calculated % N 5.57.

Sodium derivative of (III), m.p. 60-62°.



Found % N 3.40. $p\text{-}ClC_6H_4N(\overset{CH_3}{\overset{|}{C}}HCH_2OH)Na \cdot 7H_2O$. Calculated % N 3.44.

Preparation of halo derivatives. 1) Reaction of (I) with phosphorus pentachloride. To 4.3 g of the substance, contained in a small flask fitted with a reflux condenser, was added 5.2 g of phosphorus pentachloride. The reaction went violently with the evolution of heat. When the frothing had ceased the reaction mixture was heated on the boiling-water bath for 1.5 hours. At the end of heating the phosphorus oxychloride was vacuum-distilled. To identify the phosphorus oxychloride it was redistilled at atmospheric pressure, b.p. 103-106° (uncorrected). The yield of phosphorus oxychloride was 0.8 g. The residue from the distillation was extracted with ether, the ether vacuum-distilled, and the residue allowed to crystallize. In one to two days the crystalline product was freed from an oily impurity by pressing on porous plate. The yield of crude N-(β-chloroisopropyl)benzenesulfonamide was 2.5 g (53.7%), m.p. 75-77° (from petroleum ether).

Found % Cl 15.2. $C_9H_{12}O_2NClS$. Calculated % Cl 15.38.

2) Reaction of (IV) and (V) with thionyl chloride. To 1.43 g of substance (IV) or 1.5 g of substance (V), contained in a small flask fitted with a reflux condenser, was added 1.4 g of thionyl chloride. The reaction mixture was heated at 80-85° for two hours (until hydrogen chloride ceased to evolve). After reaction end, the mixture on cooling,crystallized. In the case of substance (IV) the mixture was dissolved in carbon tetrachloride, the carbon tetrachloride was vacuum-distilled, and the residue was recrystallized from petroleum ether. In the case of substance (V) the residue was recrystallized from heavy gasoline.

N-(β,β'-Dichlorodiisopropyl)-p-toluenesulfonamide (VII) was obtained in 38.2% yield, m.p. 83-87°.

Found % Cl 22.32. $C_{13}H_{19}O_2NCl_2S$. Calculated % Cl 21.6.

N-(β,β'-Dichlorodiisopropyl)-p-chlorobenzenesulfonamide (VIII) was obtained in 43.5% yield, m.p. 85-88°.

Found % Cl 29.8. $C_{12}H_{16}O_2NCl_3S$. Calculated % Cl 30.7.

Acylation of N-(β-hydroxyisopropyl)benzenesulfonamide. A mixture of 6.9 g of substance (I) and 2.4 g of acetyl chloride was heated on the boiling-water bath for two hours. The reaction mixture was poured into water, and the lower layer separated and washed with water. The residual oil was dissolved in benzene, dried, and the benzene vacuum-distilled. The residue was a sirup which could not be vacuum-distilled and could be titrated with alkali solution.

N-(β-Acetoxyisopropyl)benzenesulfonamide, $C_6H_5SO_2NHCH(CH_3)CH_2OCOCH_3$, was obtained in 65% yield.

Found: equiv. (titration with NaOH in the presence of phenolphthalein) 0.982. Calculated: equiv. 1.

SUMMARY

1. The reaction of propylene oxide with arylsulfonamides was studied.

2. Eight new arylsulfonamide derivatives were synthesized and characterized.

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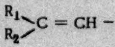
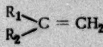
STUDY OF THE ISOMERIZATION AND DIMERIZATION OF DIMETHYLVINYLCARBINOL AS A FUNCTION OF THE pH OF THE REAGENT

IV. THE STRUCTURE OF A NEW ISOMER OF GERANIOL

A.I. Lebedeva and L.V. Kukhareva

Earlier [1] in studying the relationship between the yield of terpene alcohols and the pH of the reagent we examined the reaction of aqueous $KHSO_4$ solution with dimethylvinylcarbinol. Here a mixture of products was obtained which was not characterized completely.

This investigation was continued in the present paper; here we were able to isolate three other pure compounds, two of which proved to be identical with the unsaturated ethers obtained earlier [2], while the third was geraniol hydrate. It was shown by Pfau and Plattner [3] that the cleavage of the first molecule of water from primary-tertiary glycols, to which class geraniol hydrate belongs, occurs at the tertiary hydroxyl and the hydrogen atom found in the γ-position to the primary hydroxyl group. They assumed the structure of the terpene alcohol obtained in this manner to be identical with that of isogeraniol [4]. We dehydrated geraniol hydrate in a vacuum, with traces of $KHSO_4$, and obtained a terpene alcohol with the empirical formula $C_{10}H_{18}O$, differing in its constants from those of geraniol and linalool. When the alcohol was oxidized with chrome mixture we obtained an aldehyde, which gave a semicarbazone with m.p. 205-206°. Two moles of hydrogen were absorbed when the alcohol was hydrogenated over Pt. The saturated alcohol obtained here was identical with tetrahydrogeraniol. Ozonolysis of the $C_{10}H_{18}O$ alcohol gave, together with acetone, about 40% of formaldehyde and about 25% of formic acid. The infrared spectrum of the alcohol showed absorption bands at 837 and 890 cm^{-1}, characteristic for the "out-of-plane" C–H deformations in the groups  $\begin{matrix}R_1\\R_2\end{matrix}\!\!>C=CH-R_3$ and  $\begin{matrix}R_1\\R_2\end{matrix}\!\!>C=CH_2$, respectively. Especially characteristic was the band at 890 cm^{-1}, usually ascribed to a terminal methylene group [5]. The spectrum also showed an intense band at 1038 cm^{-1}, probably associated with the C–O vibrations in the CH_2OH group, and a band of valence vibrations (~3350 cm^{-1}).

When the $C_{10}H_{18}O$ alcohol was subjected to catalytic hydrogenation over $Pd/CaCO_3$, a halt was observed after the addition of 1 mole of hydrogen. The $C_{10}H_{20}O$ alcohol isolated as a result of the selective hydrogenation had physical constants that corresponded to those of citronellol. When the alcohol was oxidized with chrome mixture we obtained citronellic acid and its lactone, characterized as the silver salt. In its character the infrared absorption spectrum of the $C_{10}H_{20}O$ alcohol resembled that of β-citronellol, taken in the same wavelength region [6].

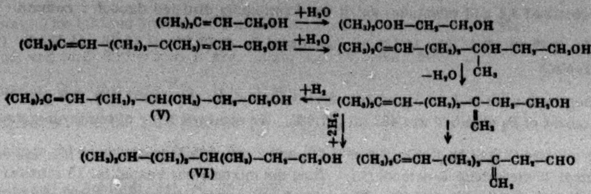
Both the absorption spectrum of β-citronellol and that of our investigated $C_{10}H_{20}O$ alcohol completely failed to show any evidence of a band at 890 cm^{-1}. Based on our studies, it can be stated that the following transformations are observed when dimethylvinylcarbinol is reacted with aqueous $KHSO_4$ solution.

1. Allylic rearrangement, leading to the formation of an equilibrium mixture of primary and tertiary alcohols.

2. Intramolecular dehydration, leading to the formation of isoprene, and intermolecular dehydration, leading to the formation of unsaturated ethers of dimethylvinylcarbinol and γ,γ-dimethylallyl alcohol.

3. Dimerization.

4. Hydration of monomeric and dimeric alcohols with the respective formation of α,α-dimethyltrimethylene glycol (I) and geraniol hydrate (II), giving on subsequent dehydration the terpene alcohol $C_{10}H_{18}O$ (III).



$$\begin{array}{lr}
(CH_3)_2C{=}CH{-}CH_2OH \xrightarrow{+H_2O} (CH_3)_2COH{-}CH_2{-}CH_2OH & (I) \\
(CH_3)_2C{=}CH{-}(CH_2)_2{-}C(CH_3){=}CH{-}CH_2OH \xrightarrow{+H_2O} (CH_3)_2C{=}CH{-}(CH_2)_2{-}\underset{CH_3}{\underset{|}{C}}OH{-}CH_2{-}CH_2OH & (II) \\
\downarrow -H_2O & \\
\underset{(V)}{(CH_3)_2C{=}CH{-}(CH_2)_2{-}CH(CH_3){-}CH_2{-}CH_2OH} \xleftarrow{+H_2} (CH_3)_2C{=}CH{-}(CH_2)_2{-}\underset{CH_2}{\underset{\|}{C}}{-}CH_2{-}CH_2OH & (III) \\
\downarrow +2H_2 \qquad \downarrow & \\
\underset{(VI)}{(CH_3)_2CH{-}(CH_2)_3{-}CH(CH_3){-}CH_2{-}CH_2OH} \quad (CH_3)_2C{=}CH{-}(CH_2)_2{-}\underset{CH_2}{\underset{\|}{C}}{-}CH_2{-}CHO & (IV)
\end{array}$$

The fact that the infrared spectrum shows a strong absorption band at 890 cm^{-1}, that ozonolysis gives formic acid in a higher than 60% yield (total), that oxidation gives the $C_{10}H_{16}O$ aldehyde (IV), that selective hydrogenation yields β-citronellol (V), and that exhaustive hydrogenation gives tetrahydrogeraniol (VI), all make it possible to assume that the cleavage of the first molecule of water from geraniol hydrate goes at least 60% with involvement of the tertiary hydroxyl group and the hydrogen of the methyl group. The main terpene alcohol obtained here is 7-methyl-3-methylene-6-octenol (III).

That the methylmethyleneoctenol is obtained as the main product in the dehydration of geraniol hydrate once again emphasizes the fact that geraniol hydrate is not an intermediate product in the interconversions of terpene alcohols [7] or in the transformations of linalool to terpineol [8].

EXPERIMENTAL

For each experiment we took 200 g of 75% dimethylvinylcarbinol and 200 ml of 20% aqueous $KHSO_4$ solution. The operating technique was the same as that used earlier [9]. The upper layer was distilled. Here the following fractions were collected: from 35 to 145°, 58.9 g (isoprene, dimethylvinylcarbinol, γ,γ-dimethylallyl alcohol); from 50 to 75° (5 mm), 19.3 g (γ,γ-dimethylallyl ether of dimethylvinylcarbinol, γ,γ-dimethylallyl ether of γ,γ-dimethylallyl alcohol); from 75 to 120° (10 mm), 15.3 g (linalool, geraniol); from 120 to 145° (7 mm), 13.4 g; residue 2.7 g. From the ether extract of the lower layer we obtained 22.4 g of mixed dimethylvinylcarbinol and γ,γ-dimethylallyl alcohol, and 2.3 g of α,α-dimethyltrimethylene glycol (see the Table).

Redistillation of the fraction with b.p. 120-145° (7 mm) gave geraniol hydrate (II) (the data are given in the Table).

Compound	Name	Empirical formula	Boiling point (pressure in mm)	d_4^{20}	n_D^{20}	MR_D		H+	Literature reference
						found	calc.		
(I)	α,α-Dimethyltrimethylene glycol	$C_5H_{12}O_2$	92—92.5° (5)	0.9649	1.4425	28.57	28.34	1.98	[1]
(II)	Geraniol hydrate	$C_{10}H_{20}O_2$	133—134 (6)	0.9436	1.4689	50.84	50.96	1.96	[3]
(VII)	3,7-Dimethyl-1,3-octanediol	$C_{10}H_{22}O_2$	127—128 (5)	0.9099	1.4475	51.14	51.43	1.98	
(III)	7-Methyl-3-methylene-6-octenol	$C_{10}H_{18}O$	68—68.5 (2) 86—87 (5)	0.8776	1.4684	48.88	48.97	0.98	[3]
(VI)	Tetrahydrogeraniol	$C_{10}H_{22}O$	95—96 (9)	0.8402	1.4391	49.55	49.90	1.06	[11,12]
(V)	Citronellol	$C_{10}H_{20}O$	82—84 (4)	0.8552	1.4465	48.75	49.43	1.03	[12]

For hydrogenation we took 2.0 g of geraniol hydrate (II), 0.2 g of Pt and 40 ml of ether. The amount of hydrogen absorbed was 262 ml (100.5%). After distilling off the ether we obtained 1.5 g of 3,7-dimethyl-1,3-octanediol (VII) (see Table).

Geraniol hydrate (II) (11.0 g) was slowly distilled in vacuo in the presence of 0.05 g of $KHSO_4$ at 85-90° (5 mm). We obtained 8.4 g of substance, which was fractionally distilled through a column.

Found %: C 77.71; H 11.83. M 153.0. Calculated %: C 77.87; H 11.76. M 154.2. (Other data are given in the Table.)

For hydrogenation we took 1.75 g of 7-methyl-3-methylene-6-octenol (III), 0.3 g of Pt and 40 ml of alcohol. The amount of H_2 absorbed was 495 ml (97.0%). We obtained 1.2 g of tetrahydrogeraniol (VI).

Chrome mixture (2 g of $Na_2Cr_2O_7$, 3 g of H_2SO_4 and 9 ml of H_2O) was added with cooling and shaking to 3.1 g of 7-methyl-3-methylene-6-octenol (III). Then the mixture was heated for 15 minutes at 60-70°, diluted with water, and neutralized with $NaHCO_3$. The neutral compounds were steam-distilled and then extracted with ether. We obtained 1.3 g of aldehyde (IV), giving the silver-mirror test. The semicarbazone had m.p. 205-206° (from alcohol).

Found %: C 63.07; H 9.32; N 20.24. $C_{11}H_{19}ON_3$. Calculated %: C 63.14; H 9.15; N 20.07.

A solution of 2.5 g of 7-methyl-3-methylene-6-octenol (III) in 30 ml of chloroform took up 1.68 g of O_3 (106.3%). The ozonide was decomposed with water, and the excess peroxide was decomposed by heating with Pt. The solution was made up to 500 ml. Aliquots were taken and found to contain 38.6% formaldehyde (with dimedon) and 25.2% formic acid. After removal of the formaldehyde the first drops of the neutral products distillate gave a precipitate of a 2,4-dinitrophenylhydrazone with m.p. 122-123°, which did not depress the mixed melting point with the 2,4-dinitrophenylhydrazone of acetone. We were unable to identify the other products of the ozonolysis.

For hydrogenation we took 2.0 g of 7-methyl-3-methylene-6-octenol (III), 1.0 g of $Pd/CaCO_3$ and 40 ml of alcohol. The amount of hydrogen absorbed was 321 ml (103.6% of the theoretical for one double bond). After removal of the alcohol by distillation we obtained 1.2 g of citronellol (V). A mixture of 1.2 g of citronellol (V), 1.5 g of $Na_2Cr_2O_7$ and 2 ml of water at 60-70° was treated in drops with 2 ml of 60% H_2SO_4. The mixture was kept at this temperature for one hour, after which it was steam-distilled. The aqueous distillate was extracted with ether, and after distilling off the ether we obtained the lactone, which was converted to the sodium salt of the acid by boiling with an excess of caustic in aqueous alcohol (1 : 1) solution. After evaporation of the alcohol and neutralization of the solution with nitric acid, the sodium salt was converted to the silver salt.

Found %: C 43.23; H 6.73; Ag 38.80. $C_{10}H_{17}O_2Ag$. Calculated %: C 43.34; H 6.18; Ag 38.92.

Another 5.0 g of citronellol (V) was oxidized repeatedly by the Tiemann-Schmidt procedure [10]. We obtained 3.1 g of neutral products (mainly the original alcohol) and 0.7 g of citronellic acid.

Found %: equiv. 170.1. $C_9H_{17}COOH$. Calculated %: equiv. 170.2.

The results given above were obtained when the silver salt was analyzed. The infrared absorption spectra were taken with an IKS-6 spectrophotometer, using a NaCl prism, and running at third speed.

SUMMARY

1. When dimethylvinylcarbinol is reacted with aqueous $KHSO_4$ solution there is observed, together with allylic rearrangement, dehydration and dimerization, also hydration, leading to the formation of α,α-dimethyltrimethylene glycol and geraniol hydrate.

2. The dehydration of geraniol hydrate in the presence of trace amounts of $KHSO_4$ gives a $C_{10}H_{18}O$ alcohol, which is mainly 7-methyl-3-methylene-6-octenol.

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SYNTHESIS OF HYDRAZIDES AND HYDRAZONES OF SOME HETEROCYCLIC AND AROMATIC ACIDS

E.S. Nikitskaia, E.E. Mikhlina, L.N. Iakhontov and V.Ia. Furshtatova

In earlier investigations [1] it had been shown that isonicotinic acid hydrazide and its derivatives (hydrazones) show substantial antituberculous activity, both in vitro and in vivo. In this connection it seemed of interest to synthesize, for testing as possible antituberculous agents, the hydrazides, and their derivatives of 4-pyridylacetic acid, β-(4-pyridyl)acrylic acid and β-(4-pyridyl)propionic acid, differing from the isonicotinoylhydrazone in having one or more methylene groups between the pyridine ring and the hydrazide radical.

It also seemed desirable to synthesize the hydrazides and hydrazones of acids belonging to the piperidine and quinuclidine series for the purpose of determining the influence exerted by the indicated rings on the biological activity of this class of compounds and to compare this activity with that shown by similar compounds of the pyridine series.

With this in mind we synthesized the hydrazides of the following acids: isonipecotic, 4-pyridylacetic, 4-piperidylacetic, β-(4-pyridyl)propionic, β-(4-piperidyl)propionic, β-(4-pyridyl)acrylic, 6-methylpicolinic and α-quinuclidinecarboxylic. Due to the fact that p-nitrobenzoic acid is close to isonicotinic acid in its chemical properties, to determine the relationship between structure and activity we also synthesized the hydrazide and some hydrazones of p-nitrobenzoic acid. To synthesize the hydrazides we reacted our earlier obtained [5, 6] ethyl esters of the mentioned acids with hydrazine hydrate in alcohol solution. Subsequent reaction of the hydrazides with various aldehydes (benzaldehyde, 4-acetamidobenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde, 4-hydroxybenzaldehyde, opianic acid) led to obtaining the hydrazones. This last reaction was run in water, aqueous alcohol or alcohol medium. The constants of the obtained compounds, their analysis and the yields are summarized in Tables 1-4.* The in vitro testing of the obtained compounds for antituberculous activity, run in the Chemotherapy Section of our Institute by O.O. Makeeva, revealed that they show considerably less activity than do the corresponding isonicotinic acid derivatives.

EXPERIMENTAL

As examples we will describe the synthesis of 6-methylpicolinic acid hydrazide, p-acetamidobenzaldehyde 6-methylpicolinoylhydrazone, benzaldehyde 4-pyridylacetylhydrazone and 4-hydroxy-3-methoxybenzaldehyde α-quinuclidinoylhydrazone.

6-Methylpicolinic acid hydrazide. To a solution of 6.5 g of ethyl 6-methylpicolinate in 10 ml of ethyl alcohol was added 4.2 g of hydrazine hydrate and the mixture heated for three hours at the boil. The alcohol and excess hydrazine hydrate were removed by distillation. The crystalline residue was pressed on a Buchner funnel and washed with anhydrous ether. We obtained 5.35 g (92%) of the compound, m.p. 91-93°.

p-Acetamidobenzaldehyde 6-methylpicolinoylhydrazone. A hot solution of 1.08 g of p-acetamidobenzaldehyde in 22 ml of water was added to a solution of 1 g of 6-methylpicolinic acid hydrazide in 5 ml of hot water. The precipitate obtained on cooling was filtered and washed with hot water. We obtained 1.78 g (91%) of the compound. M.p. 247-249° (from alcohol).

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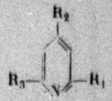
*At the time we completed the present investigation we found that some of the hydrazides prepared by us had already appeared in the literature. For this reason the proper references are included in the tables.

TABLE 1



R_1	R_2	R_3	Yield (in %)	Melting point	Analysis results (in %)					
					C		H		N	
					calc.	found	calc.	found	calc.	found
H	$CH_2CONHNH_2$	H	Quantitative	90—91°[2, 3]	55.63	55.22	5.96	5.94	27.81	27.61
H	$CH_2CH_2CONHNH_2$	H	95	61—62[3]	58.18	59.86	6.66	6.59	25.45	25.42
$CONHNH_2$	H	CH_3	92	91—93	55.63	55.41	5.96	5.91	27.81	27.46
H	$CH_2CONHN{=}CHC_6H_3$(m-OCH_3)(p-OH)	H	90	208—209	63.15	62.77	5.27	5.56	14.73	14.29
H	$CH_2CONHN{=}CHC_6H_4$(p-OH)	H	Quantitative	217—218	—	—	—	—	16.22	16.20
H	$CH_2CONHN{=}CHC_6H_4$(p-$NHCOCH_3$)	H	62**	226—227	—	—	—	—	16.91	17.03
H	$CH_2CONHN{=}CHC_6H_5$	H	84.5	116—117	—	—	—	—	17.64	17.59
H	$CH_2CH_2CONHN{=}CHC_6H_3$(m-OCH_3, p-OH)	H	86.2	212—214	64.21	64.02	5.70	5.94	14.05	13.92
H	$CH_2CH_2CONHN{=}CHC_6H_4$(p-$NHCOCH_3$)	H	89.0*	198—199	62.20	62.32	6.03	5.65	17.04	16.74
H	$CH_2CH_2CONHN{=}CHC_6H_4$(p-OH)	H	49.5	199—200	67.18	66.96	5.55	5.57	15.69	15.62
H	$CH{=}CHCONHN{=}CHC_6H_3$(m-OCH_3, p-OH)	H	57*	124—126	60.95	60.69	5.40	5.41	—	—
H	$CH{=}CHCONHN{=}CHC_6H_4$(p-$NHCOCH_3$)	H	89*	171—173	62.54	62.88	5.52	5.28	17.15	17.18
H	$CH{=}CHCONHN{=}CHC_6H_4$(p-OH)	H	69	169—171	—	—	—	—	15.73	15.67
$CONHN{=}CHC_6H_5$	H	CH_3	81	142—144	70.29	70.07	5.43	5.38	17.57	17.47
$CONHN{=}CHC_6H_2$(o-COOH), (m,pOCH_3)	H	CH_3	75	235	59.47	59.17	4.95	4.99	12.24	12.06
$CONHN{=}CHC_6H_4$(p-$NHCOCH_3$)	H	CH_3	91	247—249	64.86	65.12	5.40	5.46	18.24	18.42

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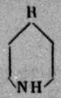
*Crystallizes with 1 H_2O.

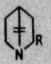
**Crystallizes with 2 H_2O.

TABLE 2



R	Yield (in %)	Melting point	Analysis results (in %)					
			C		H		N	
			calc.	found	calc.	found	calc.	found
$CONHNH_2$	83*	236—238°[2]	—	—	—	—	19.44	19.06
$CH_2CONHNH_2$	88.4*	227—228	36.52	36.67	7.39	7.55	18.26	18.25
$CH_2CH_2CONHNH_2$	96.5	70—72	—	—	—	—	24.56	24.20
$CONHN{=}CHC_6H_3(m\text{-}OCH_3)\,(p\text{-}OH)$	87**	216—217	57.16	57.16	6.80	7.15	14.28	14.30
$CONHN{=}CHC_6H_2(o\text{-}COOH)\,(m,p\text{-}OCH_3)$	78**	209	54.39	54.41	6.51	6.54	11.89	11.78
$CH_2CONHN{=}CHC_6H_3(m\text{-}OCH_3)\,(p\text{-}OH)$	90**	193—194	58.25	58.50	7.74	7.49	13.59	13.32
$CH_2CH_2CONHN{=}CHC_6H_3(m\text{-}OCH_3)(p\text{-}OH)$	88.3	223—224	62.95	62.84	7.54	7.22	—	—
$CH_2CH_2CONHN{=}CHC_6H_4(p\text{-}NHCOCH_3$	80	210—212	64.62	64.43	7.60	7.72	—	—

TABLE 3



R	Yield (in %)	Melting point	Analysis results (in %)					
			C		H		N	
			calc.	found	calc.	found	calc.	found
$CONHNH_2$	92	91—93°	56.80	56.45	8.87	8.87	24.87	24.45
$CONHN{=}CHC_6H_3(m\text{-}OCH_3)\,(p\text{-}OH)$	70**	135—138	59.81	60.00	7.16	7.[illegible]8	13.08	12.85
$CONHN{=}CHC_6H_5$	70	153—155	70.03	70.42	7.39	7.55	—	—
$CONHN{=}CHC_6H_4(p\text{-}NHCOCH_3)$	75	251—252	64.26	64.34	7.00	7.22	17.85	17.60
$CONHN{=}CHC_6H_4(p\text{-}OH)$	62**	139—141	61.85	61.85	7.21	7.08	14.43	14.99

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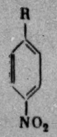
*Isolated as the dihydrochloride

**Crystallizes with 1 H_2O.

Benzaldehyde 4-pyridylacetylhydrazone. A solution of 0.15 g of benzaldehyde in 1 ml of alcohol, heated to 70°, was added to 0.23 g of 4-pyridylacetic acid hydrazide, dissolved in 1 ml of water at 70°. The solution was evaporated to dryness. The oily residue was rubbed with ether, and then with water; the obtained crystals were filtered and washed with water. We obtained 0.3 g (84.5%) of benzaldehyde 4-pyridylacetylhydrazone, m.p. 116-117°.

4-Hydroxy-3-methoxybenzaldehyde α-quinuclidinoylhydrazone. A solution of 1 g of α-quinuclidinecarboxylic acid hydrazide in 5 ml of alcohol was mixed with a solution of 0.9 g of 4-hydroxy-3-methoxybenzaldehyde in 10 ml of alcohol. Then 15 ml of water was added to the solution. The precipitate obtained on cooling in ice was filtered. We obtained 1.3 g (70%) of the compound. M.p. 136-138° (from alcohol).

TABLE 4



R	Yield (in %)	Melting point	Analysis results (in %)					
			C		H		N	
			calc.	found	calc.	found	calc.	found
CONHNH$_2$	84	208—210°[4]	46.40	46.60	3.86	3.88	23.20	23.59
CONHN=CHC$_6$H$_3$(m-OCH$_3$)(p-OH)	80*	226—227	54.05	54.09	4.50	4.54	—	—
CONHN=CHC$_6$H$_2$(o-COOH)(m,p-OCH$_3$)	75	247	—	—	—	—	11.22	11.27
CONHN=CHC$_6$H$_4$(p-OH)	86	266—268	58.94	58.83	3.85	3.86	14.73	14.84

*Crystallizes with 1 H_2O.

SUMMARY

To study the antituberculous activity we synthesized the hydrazides and some hydrazones of isonipecotic, 4-pyridylacetic, 4-piperidylacetic, β-(4-pyridyl)propionic, β-(4-piperidyl)propionic, β-(4-pyridyl)acrylic, 6-methylpicolinic, α-quinuclidinecarboxylic and p-nitrobenzoic acids.

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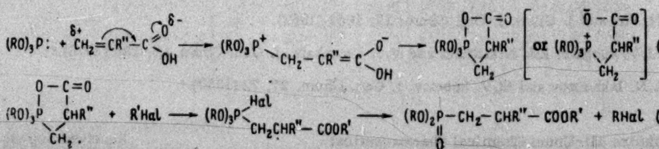
ADDITION OF NEUTRAL ESTERS OF PHOSPHOROUS AND PHOSPHONOUS ACIDS TO CONJUGATED SYSTEMS

VI. JOINT REACTION OF ALKYL HALIDES AND α,β-UNSATURATED ACIDS WITH TRIALKYL PHOSPHITES

V.A. Kukhtin and K.M. Orekhova

In earlier papers [1, 2] it had been shown that trialkyl phosphites can undergo the Arbuzov rearrangement when reacted with α,β-unsaturated acids and aldehydes. The indicated authors also established that α,β-unsaturated acids and alkyl halides are capable of joint reaction with trialkyl phosphites [3]. As a continuation of these investigations we studied the joint reaction of α,β-unsaturated acids and alkyl bromides or iodides with trialkyl phosphites. The experiments run using alkyl bromides completely confirmed the earlier-proposed scheme. As a result of these experiments we obtained the mixed esters of β-dialkylphosphonocarboxylic acids and the corresponding alkyl halides. The constants of the obtained esters are given in Table 1.

Heating was employed when methacrylic acid and alkyl bromides were jointly reacted with trialkyl phosphites. The joint reaction of acrylic acid and alkyl bromides with trialkyl phosphites proceeds more vigorously than in the case of methacrylic acid. In some cases, when the reaction was run at room temperature (Table 2, Expt. 2), the ethyl ester of β-diethylphosphonoisobutyric acid was isolated. The mixed ester could not be found in the reaction products. From this it appears that the alkyl bromide reacts with the intermediate complex mainly at elevated temperature. We studied the reaction of ethyl bromide with the intermediate product obtained as the result of adding tributyl phosphite to methacrylic acid. Butyl bromide and the ethyl ester of β-dibutylphosphonoisobutyric acid were isolated as reaction result. Consequently, the reaction can be depicted as going in two stages.

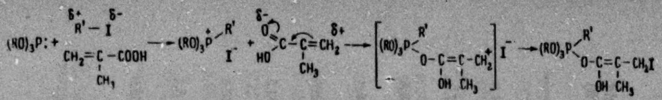


(1)

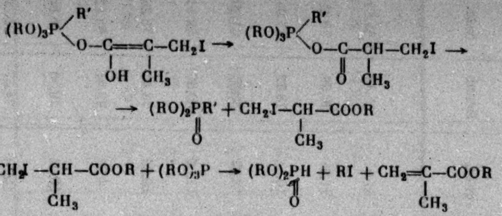
(2)

Interesting results were obtained when the joint reaction of methacrylic acid and alkyl iodides with trialkyl phosphites was studied. In this case the yields of esters of β-phosphonoisobutyric acid were small (from 8 to 18%, Table 2).

Consequently, the reaction can also go differently from the above-presented scheme. When the obtained reaction products were fractionally distilled we isolated esters of the general type $R'\underset{\underset{O}{\|}}{P}(OR)_2$, the formation of which was not observed in studying the reaction with alkyl bromides. In addition, esters of methacrylic acid and dialkylphosphorous acid were obtained as a reaction result (see Table 2). Alkyl iodides are much more active in the Arbuzov rearrangement than are the bromides, and consequently it is possible to theorize that in the first reaction stage they could compete with the methacrylic acid, in which case reaction proceeds by the scheme:



The decomposition of the unstable intermediate compound proceeds in the following manner:



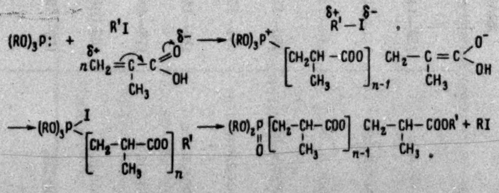
$$(\mathrm{RO})_3\mathrm{P}\begin{smallmatrix}\mathrm{R'}\\ \mathrm{O}-\end{smallmatrix}\underset{\underset{\mathrm{OH}}{|}}{\mathrm{C}}{=}\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{C}}-\mathrm{CH_2I} \rightarrow (\mathrm{RO})_3\mathrm{P}\begin{smallmatrix}\mathrm{R'}\\ \mathrm{O}-\end{smallmatrix}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{CH}}-\mathrm{CH_2I} \rightarrow$$

$$\rightarrow (\mathrm{RO})_2\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{R'} + \mathrm{CH_2I}-\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{CH}}-\mathrm{COOR}$$

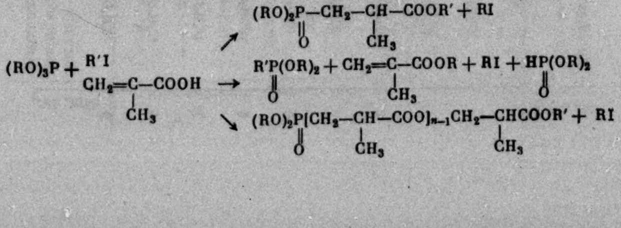
$$\mathrm{CH_2I}-\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{CH}}-\mathrm{COOR} + (\mathrm{RO})_3\mathrm{P} \rightarrow (\mathrm{RO})_2\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{H} + \mathrm{RI} + \mathrm{CH_2}{=}\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{C}}-\mathrm{COOR}$$

It is also possible for the hydrogen halide to cleave in a different manner; however, we were unable to detect the presence of hydrogen iodide in the reaction products. As a result of reaction by the above-presented scheme the following four products should be isolated: esters of general type $\mathrm{R'}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{(OR)_2}$, dialkylphosphorous acids, methacrylates and alkyl iodides. It was established that all four products are present in the reactions run by us (Table 2). The joint reaction of acrylic acid and alkyl iodides with trialkyl phosphites goes mainly by the scheme presented above for the alkyl bromides, i.e., with the formation of the corresponding esters of the β-dialkylphosphonopropionic acid. This is apparently due to the fact that acrylic acid, being more reactive, attacks the phosphite molecule before the alkyl iodide does. Then the alkyl iodide reacts with the intermediate complex formed.

In studying the joint reactions of alkyl iodides and methacrylic acid with trialkyl phosphites, the ability of trialkyl phosphites to telomerize at room temperature with methacrylic acid in the presence of alkyl iodides [3] according to the scheme was verified:



The structure of the telomerization product was not investigated. The isolated telomeric products were white, powderlike substances. They did not melt, and when heated they turned dark; they are insoluble in benzene, xylene, toluene, cyclohexane, chloroform, dioxane and carbon tetrachloride, soluble in alkalies and in methyl alcohol (when heated), and slightly soluble in acetone. Their phosphorus content ranged from 2.5 to 6.5%.



$$(\mathrm{RO})_3\mathrm{P} + \begin{smallmatrix}\mathrm{R'I}\\ \mathrm{CH_2}{=}\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{C}}-\mathrm{COOH}\end{smallmatrix} \rightarrow \begin{cases} (\mathrm{RO})_2\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}-\mathrm{CH_2}-\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{CH}}-\mathrm{COOR'} + \mathrm{RI} \\ \mathrm{R'}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{(OR)_2} + \mathrm{CH_2}{=}\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{C}}-\mathrm{COOR} + \mathrm{RI} + \mathrm{H}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{(OR)_2} \\ (\mathrm{RO})_2\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}[\mathrm{CH_2}-\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{CH}}-\mathrm{COO}]_{n-1}\mathrm{CH_2}-\underset{\underset{\mathrm{CH_3}}{|}}{\mathrm{C}}\mathrm{HCOOR'} + \mathrm{RI} \end{cases}$$

TABLE 1

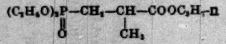
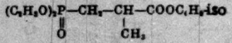
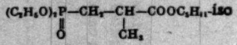
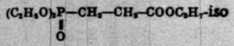
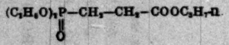
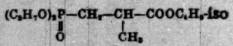
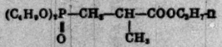
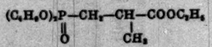
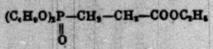
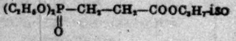
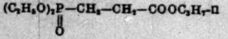
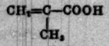
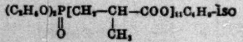
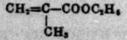
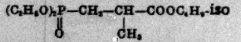
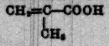
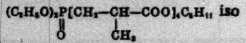
Expt. No.	Mixed ester of phosphonocarboxylic acid	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	% P		MR_D		Yield (in %)
					found	calc.	found	calc.	
1	 $(C_2H_5O)_2\underset{\underset{O}{\|}}{P}-CH_2-\underset{\underset{CH_3}{\mid}}{CH}-COOC_3H_7\text{-n}$	139—140° (8)	1.4350	1.068	11.48, 11.68	11.65	65.47	65.10	27.8
2	 $(C_2H_5O)_2\underset{\underset{O}{\|}}{P}-CH_2-\underset{\underset{CH_3}{\mid}}{CH}-COOC_4H_9\text{-iso}$	144—146 (9)	1.4360	1.052	11.09, 10.99	11.07	70.09	70.95	17.8
3	 $(C_2H_5O)_2\underset{\underset{O}{\|}}{P}-CH_2-\underset{\underset{CH_3}{\mid}}{CH}-COOC_5H_{11}\text{-iso}$	146—148 (8)	1.4310	1.001	10.32, 10.20	10.54	78.72	77.93	13.6
4	 $(C_2H_5O)_2\underset{\underset{O}{\|}}{P}-CH_2-CH_2-COOC_3H_7\text{-iso}$	150—151 (8)	1.4335	1.071	11.82, 12.09	12.22	60.85	61.20	79.0
5	 $(C_2H_5O)_2\underset{\underset{O}{\|}}{P}-CH_2-CH_2-COOC_3H_7\text{-n}$	154—156 (12)	1.4330	1.070	12.22, 12.01	12.22	60.85	59.10	52.0
6	 $(C_3H_7O)_2\underset{\underset{O}{\|}}{P}-CH_2-\underset{\underset{CH_3}{\mid}}{CH}-COOC_4H_9\text{-iso}$	164—165 (9)	1.4370	1.007	10.36, 10.10	10.22	78.43	78.28	53.5
7	 $(C_4H_9O)_2\underset{\underset{O}{\|}}{P}-CH_2-\underset{\underset{CH_3}{\mid}}{CH}-COOC_3H_7\text{-n}$	178—180 (8)	1.4410	1.023	9.92, 9.81	9.62	83.94	83.12	42.6
8	 $(C_4H_9O)_2\underset{\underset{O}{\|}}{P}-CH_2-\underset{\underset{CH_3}{\mid}}{CH}-COOC_2H_5$	180 (10)	1.4420	1.033	10.04, 9.88	10.06	79.36	78.88	8.4
9	 $(C_4H_9O)_2\underset{\underset{O}{\|}}{P}-CH_2-CH_2-COOC_2H_5$	190—192 (4)	1.4385	1.026	10.01, 10.30	10.54	74.67	75.30	55.0

TABLE 2

Expt. No.	Reactants and reaction temperature	Products isolated	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	% P found	% P calc.	MR_D found	MR_D calc.	Yield (in %)
1	$(C_2H_5O)_3P$ $CH_2{=}\underset{\substack{\vert\\ CH_3}}{C}{-}COOH$ C_3H_7Br-n 95–96°	$CH_2{=}\underset{\substack{\vert\\ CH_3}}{C}{-}COOC_2H_5$	—	1.4160	—	—	—	—	—	20.0
		$(C_2H_5O)_2POH$	72–76° (12)	1.4090	—	—	—	—	—	55.8
		$(C_2H_5O)_2\underset{\substack{\Vert\\ O}}{P}{-}CH_2{-}\underset{\substack{\vert\\ CH_3}}{CH}{-}COOC_3H_7$-n	139–140 (8)	1.4350	1.068	11.48, 11.68	11.65	65.47	64.10	27.8
2	$(C_2H_5O)_3P$ $CH_2{=}\underset{\substack{\vert\\ CH_3}}{C}{-}COOH$ C_3H_7Br-n 16°	C_3H_7Br-n	68–72	1.4320	—	—	—	—	—	88.0
		$(C_2H_5O)_2POH$	70–73 (10)	1.4080	—	—	—	—	—	19.0
		$(C_2H_5O)_2\underset{\substack{\Vert\\ O}}{P}{-}CH_2{-}\underset{\substack{\vert\\ CH_3}}{CH}{-}COOC_2H_5$	140–142 (8)	1.4340	1.081	11.90, 12.12	12.30	60.90	60.75	57.5
3	$(C_4H_9O)_3P$ $CH_2{=}\underset{\substack{\vert\\ CH_3}}{C}{-}COOH$ C_3H_7Br-n 95–96°	C_4H_9Br-n	101–102	1.4930	—	—	—	—	—	27.0
		$CH_2{=}\underset{\substack{\vert\\ CH_3}}{C}{-}COOC_4H_9$	52–52.5 (9)	1.4180	—	—	—	—	—	17.0
		$(C_4H_9O)_2POH$	114–116 (8)	1.4220	—	—	—	—	—	36.0
		$(C_4H_9O)_2\underset{\substack{\Vert\\ O}}{P}{-}CH_2{-}\underset{\substack{\vert\\ CH_3}}{CH}{-}COOC_3H_7$-n	178–180 (8)	1.4410	1.023	9.92, 9.81	9.62	83.94	83.12	42.6
4	$(C_3H_7O)_3P$ $CH_2{=}\underset{\substack{\vert\\ CH_3}}{C}{-}COOH$ C_4H_9Br-iso 95–97°	C_3H_7Br-n	68–72	1.4330	—	—	—	—	—	12.0
		$(C_3H_7O)_2\underset{\substack{\Vert\\ O}}{P}{-}CH_2{-}\underset{\substack{\vert\\ CH_3}}{CH}{-}COOC_4H_9$-iso	164.5–165 (9)	1.4370	1.007	10.36 10.10	10.07	78.43	78.28	53.5

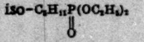
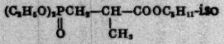
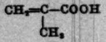
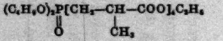
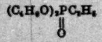
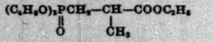
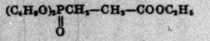
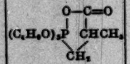
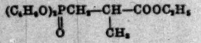
(continued)

TABLE 2 (continued)

Expt. No.	Reactants and reaction temperature	Products isolated	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	% P found	% P calc.	MR_D found	MR_D calc.	Yield (in %)
5	$(C_2H_5O)_3P$ $CH_2{=}CH-COOH$ C_3H_7Br-iso 85°	 $(C_2H_5O)_2\underset{\underset{O}{\Vert}}{P}-CH_2-CH_2-COOC_3H_7\text{-iso}$	150—151 (8)	1.4335	1.071	11.82 12.09	12.22	60.85	61.20	79.0
6	$(C_2H_5O)_3P$ $CH_2{=}CH-COOH$ C_3H_7Br-iso 20°	 $(C_2H_5O)_2\underset{\underset{O}{\Vert}}{P}-CH_2-CH_2-COOC_3H_7\text{-n}$	154.6 (12)	1.4330	1.070	12.22 12.01	12.22	60.85	59.10	52.0
7	$(C_2H_5O)_3P$  $CH_2{=}\underset{\underset{CH_3}{\vert}}{C}-COOH$ C_4H_9I-iso 15°	 $(C_2H_5O)_2\underset{\underset{O}{\Vert}}{P}[CH_2-\underset{\underset{CH_3}{\vert}}{CH}-COO]_{11}C_4H_9\text{-iso}$	—	—	—	2.39 2.59	2.72	—	—	39.2
		C_2H_5I	72—73	1.5030	—	—	—	—	—	10.6
		 $CH_2{=}\underset{\underset{CH_3}{\vert}}{C}-COOC_2H_5$	116—120	—	—	—	—	—	—	—
		$(C_2H_5O)_2POH$	72—74 (12)	1.4060	—	—	—	—	—	19.0
		 $(C_2H_5O)_2\underset{\underset{O}{\Vert}}{P}-CH_2-\underset{\underset{CH_3}{\vert}}{CH}-COOC_4H_9\text{-iso}$	144—146 (9)	1.4360	1.0520	11.09 10.99	11.19	70.09	70.95	17.8
8	$(C_2H_5O)_3P$  $CH_2{=}\underset{\underset{CH_3}{\vert}}{C}-COOH$	 $(C_2H_5O)_2\underset{\underset{O}{\Vert}}{P}[CH_2-\underset{\underset{CH_3}{\vert}}{CH}-COO]_4C_5H_{11}\text{ iso}$	—	—	—	6.03 6.13	5.61	—	—	71.8
		C_2H_5I	73—74	1.5060	—	—	—	—	—	10.6
		$(C_2H_5O)_2POH$	70—74 (10)	1.4090	—	—	—	—	—	19.0

(continued)

TABLE 2 (continued)

Expt. No.	Reactants and reaction temperature	Products isolated	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	% P		MR_D		Yield (in %)
						found	calc.	found	calc.	
8	$C_5H_{11}I$-iso	 iso-$C_5H_{11}P(O)(OC_2H_5)_2$	120—122 (8)	1.4290	—	—	—	—	—	25.0
	16°	 $(C_2H_5O)_2P(O)CH_2-CH(CH_3)-COOC_5H_{11}$-iso	146—148 (8)	1.4310	1.001	10.32, 10.20	10.54	78.72	77.93	13.6
9	(н.-$C_4H_9O)_3P$	C_4H_9J-n	130—132	1.4980	—	—	—	—	—	20.0
	 $CH_2=C(CH_3)-COOH$	 $(C_4H_9O)_2P(O)[CH_2-CH(CH_3)-COO]C_2H_5$	—	—	—	5.83, 5.25	5.55	—	—	6.8
	C_2H_5I	 $(C_4H_9O)_2P(O)C_2H_5$	135—140 (11)	1.4240	—	—	—	—	—	10.0
	16°	 $(C_4H_9O)_2P(O)CH_2-CH(CH_3)-COOC_2H_5$	180 (10)	1.4420	1.033	10.04, 9.88	10.06	79.32	78.88	8.4
10	(n-$C_4H_9O)_3P$	C_4H_9I-n	131—133	1.4905	—	—	—	—	—	20.0
	$CH_2=CH-COOH$	$(C_4H_9O)_2POH$	106—108 (5)	1.4225	—	—	—	—	—	24.0
	C_2H_5I 20°	 $(C_4H_9O)_2P(O)CH_2-CH_2-COOC_2H_5$	190—192 (4)	1.4385	1.026	10.01, 10.30	10.54	74.67	75.30	55.0
11		C_4H_9Br-n	28—29 (30)	1.4970	—	—	—	—	—	30.0
	C_2H_5Br 80°	 $(C_4H_9O)_2P(O)CH_2-CH(CH_3)-COOC_2H_5$	180—181 (9)	1.4420	1.034	—	—	—	—	58.5

The experimental results obtained by us permit making the conclusion that, depending on the experimental conditions and chemical reactivity of the reactants, the joint reaction of methacrylic acid and alkyl iodides with trialkyl phosphites can go in three directions.

EXPERIMENTAL

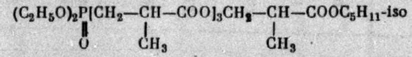
Reaction of triethyl phosphite with methacrylic acid and propyl bromide. To 15 g of triethyl phosphite and 11.1 g of propyl bromide was added 7.78 g of methacrylic acid. A rise of 2° in the temperature was observed. When heat evolution had ceased, the reaction mass was heated on the water bath (the mixture boiled at 95-96°) for six hours. Three fractional distillations gave 8 g of the propyl ester of β-diethylphosphonoisobutyric acid (Table 1, Expt. 1). The other experiments involving the reaction of alkyl bromides and methacrylic acid with trialkyl phosphites were run in a similar manner.

Reaction of ethyl bromide with the reaction product of methacrylic acid and tributyl phosphite. Methacrylic acid (9.6 g) was added in drops to 25 g of tributyl phosphite. The mixture was stirred thoroughly. After three days the reaction was considered completed (test for trivalent phosphorus with CuHal showed the absence of tributyl phosphite). Then 12.1 g of ethyl bromide was added to the reaction mass. The reaction mixture was heated on the water bath for three hours. After three fractional distillations we obtained 20 g of the ethyl ester of β-dibutylphosphonoisobutyric acid (Table 2, Expt. 11).

Reaction of triethyl phosphite with methacrylic acid and isoamyl iodide. A mixture of 20 g of triethyl phosphite, 23.8 g of isoamyl iodide and 10.3 g of methacrylic acid was allowed to stand at room temperature. After two days a white precipitate appeared in the flask, the amount of which increased with time. When reaction was complete the precipitate was filtered. The total amount of precipitate was 11.6 g, which after washing was a white powder, which did not melt, but gradually charred at 240-250°. The precipitate is insoluble in carbon tetrachloride, ether, chloroform, benzene and dioxane, slightly soluble in acetone, and readily soluble in methyl alcohol (when heated) (Table 2, Expt. 8).

Found %: C 54.60; H 7.78. P 6.03, 6.13. M 411 (ebullioscopically with methyl alcohol). $C_{25}H_{45}O_{11}P$. Calculated %: C 54.35; H 8.15; P 5.61. M 552.

The analysis data correspond to the formula



$$(C_2H_5O)_2\underset{\displaystyle O}{\underset{\|}{P}}[CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COO]_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOC_5H_{11}\text{-iso}$$

Fractional distillation of the liquid portion of the reaction products gave 2 g of ethyl iodide, 3 g of diethylphosphorous acid, 1 g of the diethyl ester of isoamylphosphonic acid and 5 g of the isoamyl ester of β-diethylphosphonoisobutyric acid. The other experiments involving the joint reaction of alkyl iodides and methacrylic acid with trialkyl phosphites were run in a similar manner.

Reaction of tributyl phosphite and acrylic acid with ethyl iodide. Acrylic acid (5.76 g) was added in drops to 20 g of tributyl phosphite and 12.5 g of ethyl iodide. The reaction went with the evolution of heat and the temperature rose to 62°. Further reaction was run at room temperature. After two days the reaction was considered complete and the material was fractionally distilled. We obtained 13 g of the ethyl ester of β-dibutylphosphonopropionic acid (Table 2, Expt. 10).

SUMMARY

1. The joint reaction of α,β-unsaturated acids and alkyl halides with trialkyl phosphites was investigated.

2. It was established that, depending on the reaction conditions and chemical reactivity of the reactants, the reaction can go in several directions.

3. Some new mixed esters of β-phosphonocarboxylic acids were obtained.

LITERATURE CITED

[1] Gil'm Kamai and V.A. Kukhtin, Proc. Acad. Sci. USSR 109, 91 (1956) ; 112, 868 (1957).*

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*Original Russian pagination. See C.B. translation.

[2] Gil'm Kamai and V.A. Kukhtin, J. Gen. Chem. 27, 2372 (1957).*

[3] V.A. Kukhtin and Gil'm Kamai, J. Gen. Chem. 28, 1196 (1958).*

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*Original Russian pagination. See C.B. translation.

1-AMINOMETHYL-4-PHTHALAZONE

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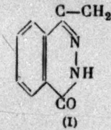
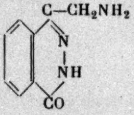
We recently obtained [1] 1-nitromethyl-4-phthalazone (I) by reacting hydrazine hydrate with 2-nitro-1,3-indandione. Since phthalazone derivatives are frequently physiologically active compounds (antituberculous agents, antihypertensives, etc.), it seemed of interest to prepare some derivatives of the nitromethylphthalazone. To obtain a water-soluble compound we reduced the nitromethylphthalazone. Various reducing agents were examined, but the best results were obtained using hydriodic acid and red phosphorus. With these reducing agents, the nitro group was smoothly reduced to the amino group, and the obtained 1-aminomethyl-4-phthalazone (II) was isolated as the hydriodide. This salt is readily soluble in water. As a compound with a primary amino group it gives a positive test with bindone [2], yields the difficultly soluble nitroindandionate [3] and reacts with phthalic anhydride [4] to give 1-phthalimidomethyl-4-phthalazone (III). The monobenzoyl derivative (IV) is formed when 1-aminomethyl-4-phthalazone is reacted with benzoyl chloride in alkaline medium, and the diacetyl derivative when (II) is reacted with acetic anhydride.

Of the three forms possible for this compound (V-VII) it appears that (VI) is the most probable. That the amino group of 1-aminomethyl-4-phthalazone acetylates is obvious from the fact that 1-phthalimidomethyl-4-phthalazone also gives an acetyl derivative (VIII), obtained as colorless crystals.


(I)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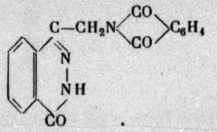
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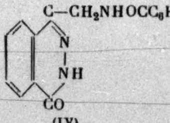
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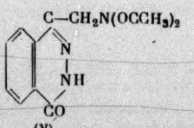
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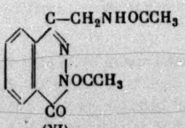
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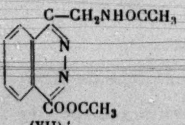
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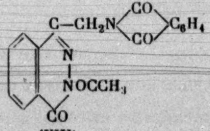
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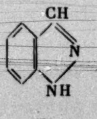
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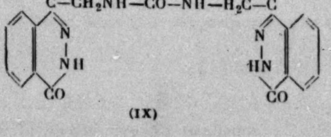
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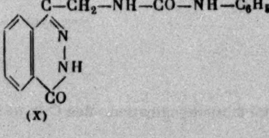
(X)

Treatment of an aqueous solution of the 1-aminomethyl-4-phthalazone hydriodide with hydrochloric acid gives a precipitate of the much less soluble hydrochloride.

We were unable to obtain the free base from the salts in a pure form. If a solution of the aminomethylphthalazone salt was treated with concentrated ammonia, then the liquid turned a reddish violet and a crystalline precipitate deposited rapidly. The filtered precipitate was nearly colorless, while the filtrate was reddish in color. The precipitate had a pyridinelike odor, and quickly deliquesced and decomposed with the evolution of ammonia. We were unable to recrystallize the free base.

When the hydrochloride of 1-aminomethyl-4-phthalazone was heated with urea in water solution, it proved that a hydrogen atom on each of the amino groups of urea was replaced by the methylphthalazone radical with the formation of N,N'-bis(4-phthalazonylmethyl)urea (IX). Only one molecule of the 1-aminomethyl-4-phthalazone reacts with phenylurea to give (X), while with N,N'-diphenylurea the reaction completely fails to go.

A white substance is formed when the nitromethylphthalazone is heated with zinc dust in a hydrogen stream, which, judging from the melting point, nitrogen content and other properties, is indazole (XI). It is entirely possible for the latter to be formed under the reaction conditions.

EXPERIMENTAL

1-Aminomethyl-4-phthalazone (II). A mixture of 1 g of 1-nitromethyl-4-phthalazone, 20 ml of hydriodic acid (b.p. 124°) and 1 g of red phosphorus was heated in a small flask under reflux for one hour. The hot solution was suction-filtered through a glass filter. The filtrate on cooling deposited lustrous crystals of the 1-aminomethyl-4-phthalazone hydriodide. The crystals were filtered, dissolved in alcohol, and precipitated with ether. Yield 1 g, m.p. 266-267° (decomp.). The compound is insoluble in other common solvents, and is readily soluble in water; it dissolves in ammonia and alkalies with a red color. The test with bindone is positive.

Found %: N 13.74; I 41.61. $C_9H_9ON_3 \cdot HI$. Calculated %: N 13.87; I 41.84.

Nitroindandionate. A saturated water solution of 1-aminomethyl-4-phthalazone hydriodide was treated with a saturated water solution of 2-nitro-1,3-indandione. A yellow crystalline precipitate of the 1-aminomethyl-4-phthalazone nitroindandionate soon deposited. The compound is insoluble in water and in alcohol. M.p. 233-235° (decomp.). For analysis the salt was washed several times with water.

Found %: N 14.83. $C_{18}H_{14}O_5N_4$. Calculated %: N 15.29.

Hydrochloride. A water solution of 1-aminomethyl-4-phthalazone hydriodide was treated with concentrated hydrochloric acid. The hydrochloride deposited as white needle crystals. After recrystallization from anhydrous alcohol, m.p. 308°.

Found %: N 19.80; Cl 17.08. $C_9H_9ON_3 \cdot HCl$. Calculated %: N 19.86; Cl 16.76.

1-Benzamidomethyl-4-phthalazone. A solution of 0.1 g of 1-aminomethyl-4-phthalazone hydriodide in 10 ml of 2% potassium hydroxide was treated with two drops of benzoyl chloride and the mixture shaken until the odor of the benzoyl chloride had disappeared. Within a few minutes the 1-benzamidomethyl-4-phthalazone deposited as fine white crystals. After recrystallization from anhydrous alcohol, m.p. 257-258°. The compound is insoluble in alkalies. When heated with alkali the compound gradually decomposes with the evolution of ammonia.

Found %: N 14.85. $C_{16}H_{13}O_2N_3$. Calculated %: N 15.05.

1-Phthalimidomethyl-4-phthalazone (III). A mixture of 1 g of 1-aminomethyl-4-phthalazone hydriodide, 2.5 g of phthalic anhydride, 0.5 g of anhydrous sodium acetate and 25 ml of glacial acetic acid was refluxed for 1.5 hours. The precipitate gradually went into solution, and then the 1-phthalimidomethyl-4-phthalazone began to deposit as a finely crystalline precipitate. The flask contents were diluted with 250 ml of water, and the mixture heated to the boil and then allowed to stand until the next day. The precipitate was separated and recrystallized from glacial acetic acid using activated carbon. M.p. 353°.

Found %: N 13.62. $C_{17}H_{11}O_3N_3$. Calculated %: N 13.77.

1-Acetamidomethyl-3-acetyl-4-phthalazone (VI). A mixture of 1 g of 1-aminomethyl-4-phthalazone hydrochloride, 2.5 g of anhydrous sodium acetate and 25 ml of acetic anhydride was refluxed for ten hours, the acetic anhydride distilled off, and the residue recrystallized from dilute methanol (1:1). M.p. 226-227°. The compound is insoluble in water, and readily soluble in alcohol; cautious dilution of the alcohol solution with water until turbidity appeared led to the deposition of long glistening needles.

Found %: N 16.60. $C_{13}H_{13}O_3N_3$. Calculated %: N 16.22.

1-Phthalimidomethyl-3-acetyl-4-phthalazone (VIII). A mixture of 1-phthalimidomethyl-4-phthalazone and acetic anhydride was refluxed for ten hours. A white crystalline precipitate was obtained on cooling. The precipitate was separated and washed with ether. M.p. 207°.

Found %: N 12.38. $C_{18}H_{13}O_4N_3$. Calculated %: N 12.54.

The compound is soluble in glacial acetic acid and alcohol, and when its solutions are boiled, a precipitate of 1-phthalimidomethyl-4-phthalazone is obtained. M.p. 353°.

N,N'-Bis(4-phthalazonylmethyl)urea (IX). A mixture of 1 g of 1-aminomethyl-4-phthalazone hydrochloride, 0.6 g of urea (mole ratio 1:2) and 100 ml of water was refluxed for four hours. A precipitate began to deposit within an hour. The compound is insoluble in cold water, alcohol and glacial acetic acid, and is soluble in alkalies. Ammonia is evolved when the compound is heated with concentrated caustic solution. After recrystallization from hot water, m.p. 320-325° with partial sublimation.

Found %: N 23.12, 22.63. $C_{19}H_{16}O_3N_6$. Calculated %: N 22.34.

Somewhat high results were frequently obtained when the compound was analyzed for nitrogen. It is obvious that here the product obtained by the condensation of the reactants in a 1:2 ratio is contaminated with the product obtained by the condensation of the reactants in a 1:1 ratio. However, we were unable to isolate the indicated compound in pure form by fractional crystallization.

N-Phenyl-N'-(4-phthalazonylmethyl)urea (X). A mixture of 1 g of the aminomethylphthalazone hydrochloride, 0.8 g of phenylurea and 60 ml of water was refluxed for two hours. We obtained 2 g of N-phenyl-N'-(4-phthalazonylmethyl)urea from the reaction. M.p. 300-301°. The compound is very difficultly soluble in alcohol, xylene, dioxane and glacial acetic acid.

Found %: N 19.15. $C_{16}H_{14}O_2N_4$. Calculated %: N 19.05.

Indazole (XI). A mixture of 1 g of the nitromethylphthalazone and 30 g of zinc dust was heated in a glass tube in a stream of hydrogen. A white deposit collected on the cold sides of the tube. The flask contents after cooling were shaken with ether, and the filtrate was evaporated. The white residue was recrystallized from water. Fine crystals with a peculiar, sweet odor. Yield 0.05 g, m.p. 140-143°.

Found %: N 23.21. $C_7H_6N_2$. Calculated %: N 23.72.

SUMMARY

The reduction of 1-nitromethyl-4-phthalazone gave 1-aminomethyl-4-phthalazone. The properties of the latter were studied, and some of its derivatives were prepared.

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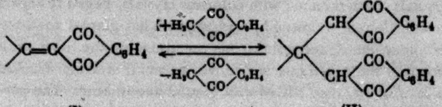
COMPOUNDS WITH TWO GEMINATE INDANDIONE GROUPS IN THE MOLECULE

II. CONDENSATION OF 5,6-DINITROACENAPHTHENEQUINONE WITH 1,3-INDANDIONE

L.S. Geita and G.Ia. Vanag

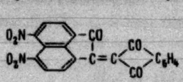
In previous papers [1-6] we had shown that many carbonyl compounds condense readily with 1,3-indandione; here, depending on the ratios of the two components, and also the reaction conditions, it is frequently possible to isolate both indandionylene derivatives of type (I) and diindandionyl derivatives of type (II). The first type usually easily add another molecule of the indandione and migrate to the second type; the latter, in turn, can cleave a molecule of the indandione and revert back to the first type.



(I) (II)

Such mutual interconversions were accomplished with the condensation products of the indandione with benzaldehyde, the nitrobenzaldehydes and acenaphthenequinone, whereas with phenanthrenequinone and nitrophenanthrenequinone only compounds of the (II) type could be obtained. In the present paper we studied the condensation of 5,6-dinitroacenaphthenequinone with 1,3-indandione.

When 5,6-dinitroacenaphthenequinone is condensed with 1,3-indandione in an equimolar ratio in glacial acetic acid the reaction goes in two directions, and both red crystals of 5,6-dinitro-2-indandionylene-1-acenaphthenone (III) and colorless crystals of 5,6-dinitro-2,2-diindandionyl-1-acenaphthenone (IV) are formed. To obtain pure (III) it is advisable to take a large amount of solvent, since colorless (IV) is somewhat more soluble in glacial acetic acid. In general, both compounds have nearly the same solubility, which makes their complete separation quite difficult. This is accomplished by repeated boiling with either chloroform or glacial acetic acid, or by careful treatment with warm pyridine. The use of alkali to separate the two compounds is not practical here, since (III) is also soluble in alkali; acidification of the solution gives an amorphous precipitate, which dissolves in sodium bicarbonate. From the literature it is known [7] that the indandione ring, devoid of an active hydrogen in the 2 position, is frequently easily cleaved by alkali with the formation of a carboxylic acid.



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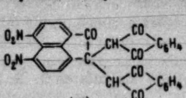

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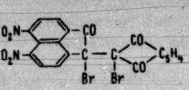

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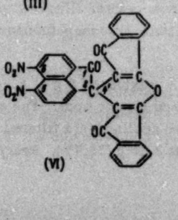

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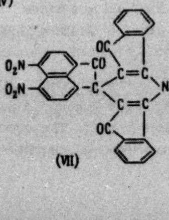

(VII)

5,6-Dinitro-2-indandionylene-1-acenaphthenone readily adds another molecule of the indandione, and here 5,6-dinitro-2,2-diindandionyl-1-acenaphthenone (IV) is formed. 5,6-Dinitro-2-indandionylene-1-acenaphthenone also adds a molecule of bromine, but the obtained dibromide (V) is unstable and again easily cleaves bromine. If dibromide (V) is treated with alcohol, then an atom of bromine still remains in the molecule. The nature of this compound has still not been determined. We were unable to add hydrobromic acid to the double bond of (III).

5,6-Dinitro-2,2-diindandionyl-1-acenaphthenone (IV), obtained by adding the indandione to 5,6-dinitro-2-indandionylene-1-acenaphthenone (III), is more conveniently obtained by the direct condensation of 5,6-dinitroacenaphthenequinone with the indandione in a 1:2 ratio in either alcohol or glacial acetic acid solution. The properties of (IV) in general resemble those of the other geminal diindandionyl derivatives studied earlier. 5,6-Dinitro-2,2-diindandionyl-1-acenaphthenone dissolves in alkalies, forming salts, but these enolic salts are difficult to isolate in the pure state. When treated with acetic anhydride, (IV) is easily cyclized to the corresponding spiro-pyran (VI). The latter reacts with difficulty with ammonia and amines, being converted to the corresponding dihydropyridines (VII). In the case of ammonia, such conversion could be effected only by reaction with liquid ammonia in a sealed tube.

EXPERIMENTAL

5,6-Dinitro-2-indandionylene-1-acenaphthenone (III). To a suspension of 1 g of 5,6-dinitroacenaphthenequinone in 50 ml of glacial acetic acid, heated to the boil, was added 1.04 g of the indandione and five drops of concentrated hydrochloric acid, and the boiling was continued. Within five minutes the starting substance had dissolved and fine red crystals, contaminated with colorless crystals, began to separate. After refluxing for 15 minutes the hot solution was filtered, followed by washing with hot glacial acetic acid and then alcohol. The crude 5,6-dinitro-2-indandionylene-1-acenaphthenone remaining on the filter weighed 0.95 g (64.6%). It was treated with a small amount of warm pyridine to remove the small amount of colorless product present. The residue was washed with alcohol and then boiled with glacial acetic acid. The pure 5,6-dinitro-2-indandionylene-1-acenaphthenone had m.p. 300-302°. The compound is soluble in pyridine and dioxane, and slightly soluble in acetone, benzene, glacial acetic acid, chloroform and alcohol; it dissolves in concentrated sulfuric acid with a bright-red color, and in alkali with a brown color.

Found %: N 6.88. $C_{21}H_8O_7N_2$. Calculated %: N 7.00.

After filtering the red crystals, the hot glacial acetic acid filtrate deposited colorless crystals of 5,6-dinitro-2,2-diindandionyl-1-acenaphthenone (IV), contaminated with a small amount of red crystals of (III).

If the above condensation is run on the water bath, then the main product is the colorless dinitrodiindandionylacenaphthenone. If the condensation is run in either somewhat dilute acetic acid solution or in alcohol, then only the colorless product is formed (see further).

5,6-Dinitro-2-indandionylene-1-acenaphthenone dibromide (V). 5,6-Dinitro-2-indandionylene-1-acenaphthenone (0.5 g) was treated with 10 ml of a glacial acetic acid solution of bromine (1:20) and the mixture boiled gently until the precipitate dissolved, which required about ten minutes. Dilution of the filtrate with water gave a white precipitate of the 5,6-dinitro-2-indandionylene-1-acenaphthenone dibromide (0.5 g). The compound melts with decomposition between 150 and 170°. The dibromide is unstable and decomposed when its recrystallization from alcohol, acetone or chloroform was attempted. It also decomposes on standing: it turns yellow and develops a bromine odor. It dissolves in concentrated sulfuric acid with a bright-red color, and in alkali with a reddish-brown color.

Found %: Br 28.88; N 4.87. $C_{21}H_8O_7N_2Br_2$. Calculated %: Br 28.57; N 5.00.

The colorless dibromide was dissolved in acetone. The orange-colored filtrate deposited fine red crystals that had m.p. 300°. Their mixture with 5,6-dinitro-2-indandionylene-1-acenaphthenone did not depress the melting point. The acetone had a strong odor of bromoacetone.

5,6-Dinitro-2,2-diindandionyl-1-acenaphthenone (IV). 1) A mixture of 2 g of 5,6-dinitroacenaphthenequinone, 50 ml of alcohol and 2.08 g of the indandione was refluxed for one hour. The solution turned dark, and fine greenish crystals began to separate from it. The crystals after cooling were filtered and washed with alcohol. The yield of 5,6-dinitro-2,2-diindandionyl-1-acenaphthenone was 3.15 g (78.7%). Recrystallization from a mixture of chloroform and alcohol gave the compound as colorless crystals with m.p. 218-220°. The compound is soluble in pyridine, chloroform and dioxane, and slightly soluble in acetone and benzene. It slowly dissolves in concentrated sulfuric acid with a red color, and in alkali with a reddish-brown color. For analysis the compound was recrystallized again from glacial acetic acid.

Found %: N 4.91, 5.24. $C_{30}H_{14}O_9N_2$. Calculated %: N 5.13.

2) A mixture of 5,6-dinitro-2-indandionylene-1-acenaphthenone, 20 ml of glacial acetic acid, 0.25 g of the indandione and several drops of concentrated hydrochloric acid was refluxed for two hours. The red crystals gradually decolorized. After washing with alcohol the colorless crystals had m.p. 219-220°. The melting point was not depressed when the crystals were mixed with the compound obtained in the preceding experiment. The same product was obtained when the condensation was run in alcohol solution.

Cleavage with concentrated sulfuric acid. One gram of 5,6-dinitro-2,2-diindandionyl-1-acenaphthenone was dissolved in 10 ml of concentrated sulfuric acid. The red solution was suction-filtered through a glass filter and then poured into approximately 300 ml of water. A dark-yellow amorphous precipitate was obtained. Recrystallization from acetone gave the compound as fine red crystals. M.p. 301°. The mixed melting point with pure 5,6-dinitro-2-indandionylene-1-acenaphthenone was not depressed.

Ammonium salt. A mixture of 1 g of 5,6-dinitro-2,2-diindandionyl-1-acenaphthenone and 25 ml of alcohol was treated with 1 ml of concentrated ammonia. The substance went into solution, and then dark-brown lustrous crystals (0.40 g) deposited from the solution. The compound was washed with alcohol and ether. M.p. 165-170°. The compound is readily soluble in alcohol, and slightly soluble in water; it decomposes when its water solutions are boiled.

Found %: N 7.11. $C_{30}H_{14}O_9N_2 \cdot NH_3$. Calculated %: N 7.46.

Piperidine salt. One gram of 5,6-dinitro-2,2-diindandionyl-1-acenaphthenone was covered with 10 ml of a 10% solution of piperidine in alcohol. The dipiperidine salt deposited from the solution as dark-brown needle crystals. M.p. 183-186°. The salt is soluble in water and in alcohol. For analysis the salt was recrystallized from alcohol.

Found %: N 7.52. $C_{30}H_{14}O_9N_2 \cdot 2C_5H_{11}N$. Calculated %: N 7.82.

5,6-Dinitro-1-acenaphthenone[2:4']spiro-2',3'(CO),6',5'(CO)-dibenzoylenepyran (VI). Two grams of 5,6-dinitro-2,2-diindandionyl-1-acenaphthenone was dissolved in 40 ml of hot acetic anhydride, 1 ml of concentrated sulfuric acid was added, and the mixture was refluxed for 15 minutes. Yellow crystals deposited. The mixture was heated another 30 minutes on the water bath. We obtained 1.3 g of 5,6-dinitro-1-acenaphthenone[2:4']spiro-2',3'(CO),6',5'(CO)-dibenzoylenepyran with m.p. 467°. The compound is soluble in nitrobenzene and pyridine, and insoluble in alkalies; it is slightly soluble in concentrated sulfuric acid with the formation of a reddish-brown color.

Found %: N 5.18. $C_{30}H_{12}O_8N_2$. Calculated %: N 5.30.

5,6-Dinitro-1-acenaphthenone[2:4']spiro-2',3'(CO),6',5'(CO)-dibenzoylene-1',4'-dihydropyridine (VII, R=H). A mixture of 0.2 g of the 5,6-dinitro-1-acenaphthenonespirodibenzoylenepyran (VI) and 5 ml of liquid ammonia was allowed to stand in a sealed ampoule for a day. The compound dissolved in the ammonia, and the liquid turned dark. The ampoule was opened, the ammonia allowed to evaporate, and the residue was recrystallized from dioxane. The dark-red crystals of 5,6-dinitro-1-acenaphthenone[2:4']spiro-2',3'(CO),6',5'(CO)-dibenzoylene-1',4'-dihydropyridine melted at 265°. The substance is soluble in nitrobenzene, dioxane, acetone, glacial acetic acid and chloroform, and is slightly soluble in alcohol.

Found %: N 8.09. $C_{30}H_{13}O_7N_3$. Calculated %: N 7.97.

SUMMARY

Depending on the conditions, the condensation of 5,6-dinitroacenaphthenequinone with 1,3-indandione gave two products: 5,6-dinitro-2-indandionylene-1-acenaphthenone and 5,6-dinitro-2,2-diindandionyl-1-acenaphthenone. The latter is easily cyclized to the corresponding spiro-pyran, and the pyran when treated with ammonia is converted to the corresponding spiro-dihydropyridine.

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β,β-DIHALOPROPIONALDEHYDES

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β,β-Dihalopropionaldehydes CHX_2CH_2CHO (I, X = Cl or Br) have not been obtained in the free state up to now. Only polymeric products were isolated by Kharasch when he attempted to hydrolyze 1,1-dihalo-3-bromo-3-acetoxypropanes $CHX_2CH_2CHBr(OCOCH_3)$ (II, X = Cl) with either acidic or alkaline agents [1].

We were also unable to obtain the aldehydes (I) by the acid hydrolysis of the corresponding acetals $CHX_2CH_2CH(OR)_2$ (III, R = alkyl) [2]; under mild conditions the acetals were recovered unchanged, while under more drastic conditions the cleavage of hydrogen halide occurred with subsequent polymerization of the formed β-haloacroleins. Reaction of (II) (X = Cl or Br) with sodium bisulfite in the presence of excess sulfur dioxide gave us the bisulfite derivatives of aldehydes (I), but their treatment with either acids or bases also failed to yield the free aldehydes (I).

As we had reported earlier [2], acetals (III) are easily converted to the corresponding 1,1,3-trihalo-3-alkoxypropanes $CHX_2CH_2CHX'(OR)$ (IV) when reacted with either phosphorus pentachloride or thionyl chloride. It was established that the shaking of these reactive compounds (IV) with water at room temperature yields homogeneous water solutions of aldehydes (I), from which the latter can be extracted with methylene chloride and then vacuum-distilled in a stream of nitrogen. Later aldehydes (I) were also obtained in a similar manner from compounds (II), but in this case the reaction went much slower and with poorer yields of the aldehyde. Both of the aldehydes (I) obtained by us are liquids with a sharp specific odor, and they both decompose rapidly, even at room temperature, with the evolution of hydrogen halide and the formation of hard polymers; hydroquinone inhibits the decomposition. β,β-Dibromopropionaldehyde is much less stable than the chloro analog, for which reason we were unable to obtain satisfactory analysis results for it.

The (I) compounds give the characteristic reactions for an aldehyde group and form the corresponding crystalline derivatives; the latter easily cleave hydrogen halide, for which reason they are unstable when stored, and melt with decomposition; they can be purified by recrystallization only if acid is absent; if such is not the case, for example, when old samples are recrystallized, the substance suffers complete conversion to the corresponding β-haloacrolein derivative.

The oxidation of (I) (X = Cl) with concentrated nitric acid gave β,β-dichloropropionic acid.

EXPERIMENTAL

Bisulfite derivative of β,β-dichloropropionaldehyde. A mixture of 7.5 g of 1,1-dichloro-3-bromo-3-acetoxypropane [1], 9.1 g of sodium metabisulfite and 25 ml of water was stirred at 80° with constant passage of sulfur dioxide until a homogeneous solution was obtained. The crystals obtained on cooling were filtered, and washed with water, alcohol and then ether. Yield 4.9 g (73%).

Found %: Na 9.80, 9.78. $C_3H_5O_4SCl_2Na$. Calculated %: Na 9.96.

Bisulfite derivative of β,β-dibromopropionaldehyde. The compound was obtained in the same manner as above. Yield 80%. The compound is much less soluble in water than the corresponding dichloro derivative.

Found %: Na 7.37, 7.39. $C_3H_5O_4SBr_2Na$. Calculated %: Na 7.19.

We were unable to obtain the corresponding β,β-dihalopropionaldehydes when the bisulfite derivatives were treated with either sodium bicarbonate solution or 1% hydrochloric acid at 35-40°, followed by extraction with methylene chloride.

β,β-Dichloropropionaldehyde

An emulsion of 10 g of 1,1,3-trichloro-3-methoxypropane [2] in 125 ml of water was shaken for three hours at room temperature, after which the water solution was separated, the residue treated with 25 ml of water, and the shaking continued for another hour, at the end of which time the amount of residue did not exceed 1.0-1.5 g. The combined water solutions were saturated with sodium chloride and then repeatedly extracted with methylene chloride. The extracts were dried over magnesium sulfate. The solvent was removed in vacuo at room temperature, and the residue was distilled in a stream of nitrogen. We obtained 5.0 g (70%) of colorless liquid with a sharp specific odor.

B.p. 43-44° (10 mm), n_D^{20} 1.4660, d_4^{20} 1.3579, MR_D 25.87; calc. 25.79.

Found %: C 28.53, 28.35; H 3.56, 3.49; Cl 54.76, 55.02. $C_3H_4OCl_2$. Calculated %: C 28.34; H 3.17; Cl 55.91.

The aldehyde was also obtained in a similar manner from 1,1-dichloro-3-bromo-3-acetoxypropane (time of hydrolysis six hours, yield 35%).

β,β-Dichloropropionaldehyde is soluble in the common organic solvents, and is insoluble in water.* On standing for one to two hours it decomposes with the evolution of hydrogen chloride and the formation of hard polymeric products; the decomposition is greatly inhibited if the compound is kept in the cold with trace amounts of hydroquinone.

The p-nitrophenylhydrazone was obtained by mixing a water solution of 0.2 g of p-nitrophenylhydrazine hydrochloride with an alcohol solution of 0.2 g of the aldehyde; for purification the reaction product was dissolved in alcohol and then precipitated with water, m.p. 101° (decomp.); soluble in alcohol and ether. The compound decomposes rapidly with the evolution of hydrogen chloride.

Found %: N 16.17, 15.81; Cl 26.80, 26.62. $C_9H_9O_2N_3Cl_2$. Calculated %: N 16.03; Cl 27.09.

The dimedone derivative was obtained by mixing a solution of 0.5 g of dimedone in 50% alcohol with an alcohol solution of 0.2 g of the aldehyde; after two days we obtained 0.4 g of white crystals, m.p. 127.5-128°.

Found %: Cl 17.99, 17.98. $C_{19}H_{26}O_4Cl_2$. Calculated %: Cl 18.25.

The bisulfite derivative was obtained by shaking an alcohol solution of the aldehyde with a water solution of sodium metabisulfite; the properties and analysis results correspond to those given above.

Semicarbazone. A water solution of 1.1 g of semicarbazide hydrochloride and 1.4 g of sodium acetate was gradually added to a solution of 1.2 g of the aldehyde in alcohol; the obtained precipitate was filtered, washed with alcohol, then with water, and immediately recrystallized from aqueous alcohol. M.p. 72-74° (decomp.).

Found %: N 22.53, 22.69; Cl 38.55, 38.74. $C_4H_7ON_3Cl_2$. Calculated %: N 22.82; Cl 38.58.

A sample of the semicarbazone, recrystallized twice from aqueous alcohol, when exposed to the air for several hours began to evolve hydrogen chloride, and here we obtained a compound with m.p. 133-134°, which from the analysis results is the semicarbazone of β-chloroacrolein.

Found %: N 28.60, 28.71; Cl 23.65, 24.46. $C_4H_6ON_3Cl$. Calculated %: N 28.34; Cl 24.02.

β,β-Dibromopropionaldehyde

Obtained in the same manner as β,β-dichloropropionaldehyde (see above) from 13.3 g of 1,1-dibromo-3-chloro-3-methoxypropane [2]. After fractional distillation in vacuo in a stream of nitrogen we obtained 6.5 g (60%) of the compound.

B.p. 49.5-50° (2.5 mm), n_D^{20} 1.5385, d_4^{20} 2.0769, MR_D 32.40; calc. 31.60.

The aldehyde has a sharp specific odor, is extremely unstable, and decomposes rapidly with the evolution of hydrogen bromide and the formation of hard polymeric products.

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*Aldehydes (I) after extraction, drying and distillation, are insoluble in water, although homogeneous solutions (either the hydrated form or the polyacetal?) are formed when the (II) compounds are hydrolyzed.

Found % C 17.96, 18.14; H 2.04, 2.24; Br 72.78, 73.05. $C_3H_4OBr_2$. Calculated % C 16.76; H 1.86; Br 74.02.

The p-nitrophenylhydrazone was obtained by mixing an alcohol solution of 0.5 g of β,β-dibromopropionaldehyde with a water solution of 0.5 g of p-nitrophenylhydrazine hydrochloride. Yield 0.45 g, m.p. 80-82° (decomp.).

Found % N 11.79, 11.68. $C_9H_9O_2N_3Br_2$. Calculated % N 11.97.

The compound decomposes when its recrystallization is attempted; when kept in the air it changes rapidly with the evolution of hydrogen bromide.

Dimedon derivative, m.p. 119-120°.

Found % Br 33.36, 33.37. $C_{19}H_{26}O_4Br_2$. Calculated % Br 33.47.

The bisulfite derivative was obtained by shaking an alcohol solution of the aldehyde with a water solution of sodium metabisulfite; the properties and analysis results correspond with those described above.

Semicarbazone. A water solution of 0.25 g of semicarbazide hydrochloride and 0.35 g of sodium acetate was added gradually to a solution of 0.5 g of the aldehyde in alcohol. We obtained 0.55 g of the semicarbazide with m.p. 124.5-126° (decomp.).

Found % N 15.63, 15.69. $C_4H_7ON_3Br_2$. Calculated % N 15.38.

After recrystallization from aqueous alcohol, a sample of the semicarbazone was allowed to stand in the air for several hours, and here we obtained a substance with m.p. 138.5° (decomp.), which from the analysis results is the semicarbazone of β-bromoacrolein.

Found % N 22.07, 22.06. $C_4H_6ON_3Br$. Calculated % N 21.87.

Oxidation of β,β-dichloropropionaldehyde. β,β-Dichloropropionaldehyde (3.2 g) was added slowly to 5 ml of nitric acid (d 1.48). A copious evolution of nitrogen oxides began within 30 minutes. The next day the mixture was cautiously heated on the water bath for seven hours until all of the nitrogen oxides had been removed, after which it was diluted with water, and then extracted with ether and methylene chloride. The residue after evaporating the solvents was fractionally distilled in vacuo. We obtained 1.5 g (41%) of β,β-dichloropropionic acid with b.p. 76-78° (1.5 mm), which crystallized completely on cooling; m.p. 54.5-55° (from petroleum ether) [3].

SUMMARY

The new β,β-dichloro- and β,β-dibromopropionaldehydes were obtained by the hydrolysis of 1,1,3-trihalo-3-alkoxypropanes under mild conditions and their properties were characterized. The derivatives of these aldehydes easily lose hydrogen halide, being converted to the corresponding β-haloacrolein derivatives.

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N-ARYLSULFONAMIDE DERIVATIVES OF DIETHANOLAMINE

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Substituted ethanolamines have received much discussion in the literature, especially in review papers and monographs. The arylsulfonamide derivatives of monoethanolamine and diethanolamine have hardly been studied.

The purpose of the present investigation was to synthesize and study the properties of the indicated type of compounds, and first those derived from diethanolamine and arylsulfonyl chlorides.

$$ArSO_2Cl + 2HN(CH_2CH_2OH)_2 \rightarrow ArSO_2N(CH_2CH_2OH)_2 + HCl \cdot HN(CH_2CH_2OH)_2$$

The N,N-bis(2-hydroxyethyl)arylsulfonamides formed according to this reaction, as well as their derivatives, should undoubtedly possess practical interest. From the literature it is known that the neutral esters of these compounds, as well as the esters of N-alkyl-N-(2-hydroxyethyl)arylsulfonamides, have been suggested useful as plasticizers and waxes [1, 2].

N,N-Bis(2-hydroxyethyl)-p-toluenesulfonamide was synthesized from ethylene chlorohydrin and the sodium derivative of p-toluenesulfonamide, going through N-(2-hydroxyethyl)-p-toluenesulfonamide. Here the product was obtained in 18% yield as a slowly crystallizing viscous sirup [3]. Some information is given in one of the patents on the preparation of N,N-bis(2-hydroxyethyl)-p-toluenesulfonamide and N,N-bis(2-hydroxyethyl)-2-naphthalenesulfonamide from diethanolamine and the proper arylsulfonyl chloride in the presence of aqueous soda solution [2]. The compounds obtained using this method frequently differ in their properties from those synthesized by us.

We synthesized the following N,N-bis(2-hydroxyethyl)arylsulfonamides:

$$ArSO_2N(CH_2CH_2OH)_2$$

$$\text{(I) } Ar = C_6H_5,\ \text{(II) } Ar = C_6H_4Cl\text{-}p,\ \text{(III) } Ar = C_6H_4NO_2\text{-}p,\ \text{(IV) } Ar = C_6H_4CH_3\text{-}p,\ \text{(V) } Ar = C_6H_4CH_3\text{-}o;$$
$$\text{(VI) } Ar = C_6H_3ClNO_2\text{-}1, 2,\ \text{(VII) } Ar = \beta\text{-}C_{10}H_7.$$

To synthesize N,N-bis(2-hydroxyethyl)benzenesulfonamide and N,N-bis(2-hydroxyethyl)-p-chlorobenzenesulfonamide we first used the method of heating equimolar amounts of the sulfonyl chloride and amine in the presence of one equivalent of aqueous caustic solution [4]. However, we were unable to obtain the desired products with this procedure. In the case of benzenesulfonyl chloride we isolated a substance with m.p. 128°, apparently of the same composition as $(C_6H_5SO_2OCH_2CH_2)_2NSO_2C_6H_5$, as the calculated N for this compound is 2.66%, while the obtained product had 2.8% N.

The attempted synthesis of diethanolamine derivatives of arylsulfonamides from equimolar amounts of diethanolamine and the proper arylsulfonyl chloride in the presence of pyridine (based on the well-known reaction [1, 5]) also gave negative results.

In the case of p-chlorobenzenesulfonyl chloride we isolated here a pure high-melting, nitrogen-free compound, in its composition corresponding to the sodium salt of p-chlorobenzenesulfonic acid. Only N,N-bis(2-hydroxyethyl)-2-naphthalenesulfonamide was obtained with this procedure in 25% of the theoretical yield.

The other compounds were synthesized by a new method, based on the reaction of a double amount of diethanolamine with the proper arylsulfonyl chloride in the absence of a base, with refluxing in o-xylene for five hours.

With the exception of the o-toluenesulfonamide derivative, the N,N-bis(2-hydroxyethyl)arylsulfonamides are crystalline compounds. They are all insoluble in alkalies, in cold water and in petroleum ether, are easily soluble in acetone and alcohol, soluble in boiling benzene, and slightly soluble in carbon tetrachloride. They were purified by recrystallization from a suitable solvent.

To prove the structure of the synthesized compounds we studied some of their chemical properties, and specifically the preparation of the chlorides and bromides. We used thionyl chloride [3] to replace the hydroxyl group by chlorine, since the other methods examined proved to be less suitable. To replace the hydroxyl group by bromine we reacted a solution of the N,N-bis(2-hydroxyethyl)arylsulfonamide with gaseous hydrogen bromide.

The following halo derivatives of N,N-bis(2-hydroxyethyl)arylsulfonamides were prepared:

$$ArSO_2N(CH_2CH_2X)_2$$

(VIII) Ar = C_6H_5, X = Cl; (IX) Ar = C_6H_4Cl-n, X = Cl; (X) Ar = $C_6H_4CH_3$-o, X = Cl;
(XI) Ar = C_6H_5, X = Br; (XII) Ar = $C_6H_4NO_2$-p, X = Br.

All of the obtained halo derivatives of N,N-bis(2-hydroxyethyl)arylsulfonamides are crystalline compounds. They are insoluble in water, readily soluble in acetone, carbon tetrachloride and benzene and more difficultly soluble in alcohol and petroleum ether. The bromides attack the mucous membranes of the eyes and nose.

EXPERIMENTAL

Reaction of Diethanolamine with Arylsulfonyl Chlorides

A. A mixture of 0.05 mole of arylsulfonyl chloride, 0.11 mole of diethanolamine and 25-30 ml of o-xylene was boiled for five hours in a flask fitted with a reflux condenser and mechanical stirrer. The reaction mass after cooling was removed from the flask, and the o-xylene solution was separated in a separatory funnel (a precipitate was obtained in the case of p-chlorobenzenesulfonyl chloride, which was filtered and treated with 10% sodium hydroxide solution). The residual sirupy liquid was treated with 10% sodium hydroxide solution and the obtained precipitate was filtered. In the case of the benzene-, p-toluene- and o-toluenesulfonyl chlorides,an emulsion was formed with the caustic solution, which had to be decomposed with acid, and then the compound was separated in conventional manner. The precipitate was filtered, dried and recrystallized. The compounds obtained as viscous oils were washed with water, dissolved in acetone, the solution dried over fused potash, and the acetone vacuum-distilled. The derivative, obtained from benzenesulfonyl chloride in this manner, crystallized after standing for ten days.

To obtain an accurate accounting of the reaction products, the alkaline filtrate was acidified under cooling with concentrated hydrochloric acid until acid to Congo, then evaporated in vacuo, the residue dissolved in a mixture of alcohol and acetone, the sodium chloride separated, and the solvents removed by vacuum-distillation. The residual thick, colored liquid contained excess diethanolamine and secondary reaction products, which were not investigated. The xylene was removed from the o-xylene solution by vacuum-distillation.

The following compounds were synthesized with the indicated procedure:

N,N-Bis(2-hydroxyethyl)benzenesulfonamide (I), yield 74.3%, m.p. 60-64° (from carbon tetrachloride).

Found %: N 5.76. $C_{10}H_{15}O_4NS$. Calculated %: N 5.71.

N,N-Bis(2-hydroxyethyl)-p-chlorobenzenesulfonamide (II), yield 79.9%, colorless scales, m.p. 88-89° (from benzene).

Found %: N 5.10. $C_{10}H_{14}O_4NSCl$. Calculated %: N 5.00.

N,N-Bis(2-hydroxyethyl)-p-nitrobenzenesulfonamide (III), yield 32.2%, yellow crystals with m.p. 128-130° (from n-butyl alcohol).

Found %: N 9.30. $C_{10}H_{14}O_6N_2S$. Calculated %: N 9.60.

N,N-Bis(2-hydroxyethyl)-p-toluenesulfonamide (IV), yield 84.9%, colorless crystals with m.p. 101.5-103° (from water).

Found %: N 5.60. $C_{11}H_{17}O_4NS$. Calculated %: N 5.40.

N,N-Bis(2-hydroxyethyl)-o-toluenesulfonamide (V), yield 94.6%, clear amber sirup.

Found % N 5.66. $C_{11}H_{17}O_4NS$. Calculated % N 5.40.

N,N-Bis(2-hydroxyethyl)-1,2-chloronitrobenzenesulfonamide (VI), yield 21%, yellow crystals, m.p. 145-146° (from ethanol).

Found % N 8.63; S 10.40. $C_{10}H_{13}O_6N_2ClS$. Calculated % N 8.62; S 9.86.

To increase the yield of N,N-bis(2-hydroxyethyl)-1,2-chloronitrobenzenesulfonamide we ran experiments in which the time of heating in o-xylene was increased to ten hours, and also experiments in which the 1,2-chloronitrobenzenesulfonamide was added slowly in drops to the reaction sphere. These experiments failed to improve the results.

B. A mixture of 0.05 g-mole of 2-naphthalenesulfonyl chloride, 0.05 g-mole of diethanolamine, 4.0 ml of anhydrous pyridine and 25 ml of o-xylene was boiled for five hours in a flask fitted with a reflux condenser and mechanical stirrer. The reaction mixture was worked up in conventional manner. The condensation product was isolated from solution after distilling off the solvents in vacuo. The N,N-bis(2-hydroxyethyl)-2-naphthalenesulfonamide (VII) (yield 25%) was recrystallized from petroleum ether, m.p. 135-138°.*

Found % N 4.55. $C_{14}H_{17}O_4NS$. Calculated % N 4.74.

Preparation of Halo Derivatives

To prepare the chloro derivatives the N,N-bis(2-hydroxyethyl)arylsulfonamide (I – 0.004 g-mole, II – 0.0107 g-mole, V – 0.015 g-mole) was charged into a small reaction flask fitted with stirrer, dropping funnel, thermometer and reflux condenser, and then thionyl chloride (respectively, 0.0096, 0.026 and 0.037 g-mole) was added in drops and with good cooling. The temperature of the reaction mixture was not allowed to exceed 10°. After all of the thionyl chloride had been added, the stirring and cooling was continued for another four hours, after which the reaction mixture was allowed to stand overnight. The next day the mixture was heated at 60-70° for two hours, and at 100° for one hour. Then the reaction mixture was cooled and poured into cold water. The solid product was filtered, washed thoroughly with water, dried and recrystallized. A viscous liquid was obtained from N,N-bis(2-hydroxyethyl)-o-toluenesulfonamide, which failed to solidify on long cooling. The liquid was washed with water, dissolved in benzene, the solution dried over anhydrous sodium sulfate, and the benzene vacuum-distilled. The yield of pure chloride was 22.1%. After recrystallization from petroleum ether, N,N-bis(2-chloroethyl)benzenesulfonamide (VIII) had m.p. 47-48° [6].

Found % N 5.03. $C_{10}H_{13}O_2NCl_2S$. Calculated % N 4.96.

N,N-Bis(2-chloroethyl)-p-chlorobenzenesulfonamide (IX), yield 18.0%, m.p. 84-85° (from petroleum ether) [6].

Found % S 10.35; Cl 33.52. $C_{10}H_{12}O_2NCl_3S$. Calculated % S 10.11; Cl 33.64.

N,N-Bis(2-chloroethyl)-o-toluenesulfonamide was obtained as a dark-yellow sirup. The yield of technical chloride was 51.75%.

Found % Cl 22.90. $C_{11}H_{15}O_2NCl_2S$. Calculated % Cl 23.90.

To synthesize the bromo derivatives we dissolved 0.004 g-mole of N,N-bis(2-hydroxyethyl)benzenesulfonamide in 10 ml of hydrobromic acid, and 0.0008 g-mole of N,N-bis(2-hydroxyethyl)-p-nitrobenzenesulfonamide in 10 ml of o-xylene; gaseous hydrogen bromide was then passed through the respective solutions for two hours with heating (on the boiling-water bath), after which the reaction mixtures were allowed to stand overnight. The bromide formed in the first experiment was filtered, washed thoroughly with water, dried, and recrystallized from methyl alcohol. To isolate the second bromide the o-xylene solution was evaporated in vacuo; the residue washed with water, dried, and then recrystallized from methyl alcohol.

N,N-Bis(2-bromoethyl)benzenesulfonamide (XI) was obtained in 35.4% yield, and had m.p. 94-95°.

Found % Br 44.33. $C_{10}H_{13}O_2NBr_2S$. Calculated % Br 43.96.

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*From the literature [2]: m.p. 92-94°.

N,N-Bis(2-bromoethyl)-p-nitrobenzenesulfonamide (XII) was obtained in 31.0% yield, and had m.p. 152-153°.

Found %: S 7.32. $C_{10}H_{12}O_4N_2Br_2S$. Calculated %: S 7.69.

The obtained yields of the bromides cannot be considered as being the maximum, since the losses incurred in working with small amounts of materials were relatively great.

SUMMARY

1. The condensation of diethanolamine with arylsulfonyl chlorides was investigated, and a new method for the synthesis of N,N-bis(2-hydroxyethyl)arylsulfonamides was proposed.

2. It was shown that in the presence of aqueous caustic, or of pyridine, the reaction to give N,N-bis(2-hydroxyethyl)arylsulfonamides either does not go or it leads to the formation of quite impure products.

3. Ten new arylsulfonamide derivatives were synthesized and characterized.

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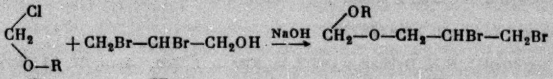
ETHERS OF GLYCOLS AND THEIR DERIVATIVES

XXXV. SYNTHESIS OF β,γ-DIBROMO DERIVATIVES OF ETHERS OF METHYLENE GLYCOL

Shamkhal Mamedov and D. Khydyrov

One of us had proposed a method for the synthesis of both symmetrical and unsymmetrical methylene glycol ethers [1].

In this paper the method was applied to the preparation of the β,γ-dibromo derivatives of methylene glycol ethers, which, as is known from the literature, have remained completely unstudied. The reaction can be depicted by the scheme.



$$\underset{(I)}{CH_2\begin{matrix}\diagup Cl\\ \diagdown O-R\end{matrix}} + \underset{(II)}{CH_2Br-CHBr-CH_2OH} \xrightarrow{NaOH} \underset{(III)}{\overset{\diagup OR}{CH_2}-O-CH_2-CHBr-CH_2Br}$$

β,γ-Dibromopropyl alcohol (II) has received little study, and the data given in the literature regarding its nature and constants are contradictory [2].

Our experiments on the matter revealed that the β,γ-dibromopropyl alcohol obtained by us under the generally known conditions [3-9], also used by V.D. Iasnopol'skii in his attempted preparation of the alcohol [2], contrary to the data given by Iasnopol'skii, distills at 213-214° at atmospheric pressure, with considerable decomposition. The constants of the pure product, obtained by vacuum-distillation, are quite different from those given in Iasnopol'skii's paper.

In his paper, Iasnopol'skii states that the reaction of the β,γ-dibromopropyl alcohol obtained by him with benzoyl chloride enabled him to obtain the benzoate of β,γ-dibromopropyl alcohol (V) with m.p. 86-88°. However, he failed to support his conclusions by any analytical data, limiting himself only to a melting point determination of the obtained product. For this reason we decided to repeat this portion of V.D. Iasnopol'skii's work, and must confess that all of the conclusions given by Iasnopol'skii in the indicated paper are entirely different from the actuality.

Further, Iasnopol'skii writes that he was able to synthesize a new cyclic ester from the β,γ-dibromopropyl benzoate obtained by him. However, verification of the author's data (0.1310 g substance, 21.25 g benzene, Δ^t 0.174°) revealed that he made an error in the calculations, for the molecular weight found by the author is actually equal to 182.2, and not 321.6, as given in the paper for the cyclic ester.

We were able to synthesize β,γ-dibromopropyl benzoate (V) by reacting benzoyl chloride with β,γ-dibromopropyl alcohol, and the compound proved to be an oily liquid, and not the crystalline product with m.p. 86-88°, as indicated by V. Iasnopol'skii.

The composition of the dibromo ester (V) obtained by us was established by complete elemental analysis and determination of the molecular weight, while the structure was established by saponification with alkali.

In addition, to verify the obtained data, we synthesized β,γ-dibromopropyl benzoate (V) by the bromination of allyl benzoate (IV) in the cold.

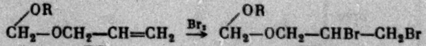
$$\underset{(IV)}{C_6H_5COOCH_2{-}CH{=}CH_2} \xrightarrow{Br_2} \underset{(V)}{C_6H_5COOCH_2{-}CHBr{-}CH_2Br}$$

The constants of the esters, obtained by the two methods, showed complete agreement.

Consequently, the reported synthesis of a cyclic ester (ester of 1-hydroxymethylcyclopropane-2,2-dicarboxylic acid) by V. Iasnopol'skii also proved to be erroneous, since the starting material that the author used in the Perkin synthesis was actually not suitable.

Having answered some of the questions connected with β,γ-dibromopropyl alcohol (being the starting material in our subsequent syntheses), we synthesized a number of alkyl β,γ-dibromopropyl ethers of methylene glycol (III), this being the main purpose of our study, and established that these ethers are readily obtained in 40% yield by reacting α-chloro ethers (I) with β,γ-dibromopropyl alcohol (II) in anhydrous benzene in the presence of 70% NaOH. The composition of the synthesized dibromo ethers (III) was shown by their complete analysis, while the structure was shown by hydrolysis, which led to the formation of β,γ-dibromopropyl alcohol, formaldehyde and the corresponding alcohols.

To verify the obtained data we synthesized the dibromo ethers (III) by the bromination of the unsaturated alkyl allyl ethers of methylene glycol (VI) in the cold.



$$\underset{(VI)}{\overset{OR}{CH_2}{-}OCH_2{-}CH{=}CH_2} \xrightarrow{Br_2} \underset{(III)}{\overset{OR}{CH_2}{-}OCH_2{-}CHBr{-}CH_2Br}$$

The constants of the dibromo ethers, obtained by the two methods, showed complete agreement.

EXPERIMENTAL

Synthesis of β,γ-dibromopropyl alcohol (II). Bromine (100 g) was added in drops, with vigorous stirring and cooling (ice + salt), to 36 g of allyl alcohol. After washing and drying, the reaction products were fractionally distilled in vacuo to give 108 g (80%) of β,γ-dibromopropyl alcohol (II).

B.p. 213-214° (decomp.), 117-119° (17 mm), d_4^{20} 2.1569, n_D^{20} 1.5625, MR_D 32.8; calc. 33.11.

Literature [3, 8, 10]: b.p. 118° (17 mm), 219° (decomp.), d^{*} 2.1682.**

Found %: C 17.17; H 2.93; Br 73.42. $C_3H_6OBr_2$. Calculated %: C 16.52; H 2.75; Br 73.39.

Synthesis of β,γ-dibromopropyl benzoate (V). A mixture of 145 g of benzoyl chloride, 218 g of β,γ-dibromopropyl alcohol and 300 g of anhydrous benzene was treated dropwise with 60 ml of 70% NaOH (in 35 minutes), with stirring and cooling (ice + salt). The stirring was continued for two hours with cooling and then for 30 minutes at 60-70°. After washing, drying and removal of the solvent we obtained 206 g of an oily liquid, from which we obtained 180 g (56%) of β,γ-dibromopropyl benzoate (V) by two vacuum-distillations.

B.p. 155-157° (4 mm), f.p. −18°; d_4^{20} 1.6890, n_D^{20} 1.5692, MR_D 62.48; calc. 61.96.

Found %: C 37.23, 37.25; H 3.17, 3.20; Br 49.05, 49.30. M 321.4. $C_{10}H_{10}O_2Br_2$. Calculated %: C 37.26; H 3.11; Br 49.69. M 322.

Synthesis of allyl benzoate (IV). A 50% NaOH solution (90 g) was added with stirring at room temperature to a mixture of 58 g of allyl alcohol, 147 g of benzoyl chloride and 200 ml of anhydrous benzene. After the usual workup we obtained 89 g (55%) of allyl benzoate (IV).

B.p. 118-120° (21 mm), d_4^{20} 1.0556, n_D^{20} 1.5192, MR_D 46.62; calc. 45.97.

Literature [11]: b.p. 228°, d_4^{4} 1.0671, d_{15}^{15} 1.0578.

Found %: C 73.82, 73.77; H 6.27, 6.30. $C_{10}H_{10}O_2$. Calculated %: C 74.07; H 6.17.

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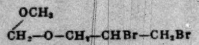
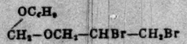
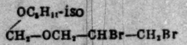
*As in original — Publisher's note.

**The constants given in V. Iasnopol'skii's paper [2] for β,γ-dibromopropyl alcohol (b.p. 205.5-206°, d_4^{20} 1.8960; n_D^{20} 1.5360) do not agree with either the literature or our data.

Alkyl β,γ-Dibromopropyl Ethers of Methylene Glycol (III)

Compound No.	Structure and name of obtained ethers	Boiling point and pressure (in mm)	d_4^{20}	n_D^{20}	MR_D		Amount (in %)						Yield (in %)
							C		H		Br		
					found	calc.	found	calc.	found	calc.	found	calc.	
1	 $\overset{OCH_3}{CH_2}-O-CH_2-CHBr-CH_2Br$ Methyl-β,γ-dibromopropyl ether of methylene glycol	129—130.5° (34)	1.7776	1.5074	43.90	44.11	—	—	—	—	61.41, 61.46	61.07	38
2	 $\overset{OC_4H_9}{CH_2}-OCH_2-CHBr-CH_2Br$ Butyl-β,γ-dibromopropyl ether of methylene glycol	117—118 (3)	1.5136	1.4904	58.13	57.96	32.10, 31.29	31.58	5.42, 5.28	5.26	52.21, 52.28	52.63	40
3	 $\overset{OC_5H_{11}\text{-iso}}{CH_2}-OCH_2-CHBr-CH_2Br$ Isoamyl-β,γ-dibromopropyl ether of methylene glycol	119—120 (4)	1.4532	1.4860	62.83	62.58	—	—	—	—	50.03, 50.23	50.32	42

Bromination of allyl benzoate (IV). Bromine (24 g) was added with strong cooling (−15°) and stirring to a solution of 24 g of the benzoate in 100 ml of anhydrous ether. After washing, drying and removal of the solvent by distillation we obtained 38.5 g (80%) of β,γ-dibromopropyl benzoate (V).

B.p. 150-151° (3 mm), d_4^{20} 1.6865, n_D^{20} 1.5704, MR_D 62.69. $C_{10}H_{10}O_2Br$. Calculated 61.96.

Saponification of β,γ-dibromopropyl benzoate (V). A mixture of 8.5 g of benzoate (V) and 20 ml of 20% KOH was heated for one hour, after which the mixture was acidified with dilute hydrochloric acid. We obtained 2 g of benzoic acid and 2.5 g of unchanged β,γ-dibromopropyl benzoate.

Synthesis of butyl β,γ-dibromopropyl ether of methylene glycol. A mixture of 88 g of β,γ-dibromopropyl alcohol (II), 53 g of α-chloromethyl butyl ether, obtained by the Litterscheid procedure [12], and 150 g of anhydrous benzene was treated with 40 ml of 50% NaOH solution at 20° and with vigorous stirring. After washing, drying and removal of the benzene by distillation we obtained 49 g (40%) of the butyl β,γ-dibromopropyl ether of methylene glycol, the constants of which are given in the Table (Compound 2).

We also isolated 10 g of the dibutyl ether of methylene glycol from the reaction products, while 3 g of a heavy tarry product remained in the distillation flask. Using similar conditions we synthesized two other new ethers, the constants of which are given in the Table.

Synthesis of butyl allyl ether of methylene glycol (VI). This unsaturated ether was synthesized using the alkaline method of synthesizing glycol ethers [1].

B.p. 75-77° (40 mm), d_4^{20} 0.8488, n_D^{20} 1.4102, MR_D 42.05. $C_8H_{16}O_2$. Calc. 41.97.

Found % C 66.50; H 11.13. M 143.8. $C_8H_{16}O_2$. Calculated % C 66.67; H 11.11. M 144.

Bromination of butyl allyl ether of methylene glycol (VI). The bromination was run by the method described above. We obtained 23.5 g (55%) of the butyl β,γ-dibromopropyl ether of methylene glycol, the constants of which showed complete agreement with the data given in the Table (Compound 2).

Hydrolysis of the butyl β,γ-dibromopropyl ether of methylene glycol (III). The hydrolysis of 19.7 g of dibromo ether (III) was run in conventional manner. From the hydrolysis we isolated 2 g of butyl alcohol and 10 g of β,γ-dibromopropyl alcohol (V). The black residue in the distillation flask weighed 1 g.

SUMMARY

1. It was established that the β,γ-dibromopropyl derivatives of methylene glycol ethers can be synthesized by the alkaline method of synthesizing glycol ethers.

2. A method was proposed for the synthesis of the β,γ-dibromopropyl derivatives of methylene glycol ethers by the bromination of the alkyl allyl ethers of methylene glycol.

3. Three new β,γ-dibromopropyl derivatives of methylene glycol ethers were synthesized and some of their properties were studied.

4. The constants given in the literature [2] for β,γ-dibromopropyl alcohol and β,γ-dibromopropyl benzoate were corrected.

5. Two different methods were offered for the synthesis of β,γ-dibromopropyl benzoate.

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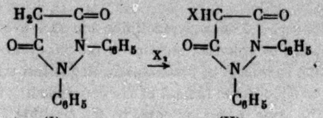
CHEMISTRY OF PYRAZOLIDINE

II. HALOGENATION AND THIOCYANATION OF 1,2-DIPHENYL-3,5-DIOXOPYRAZOLIDINE AND ITS DERIVATIVES

V.G. Pesin, A.M. Khaletskii and Teng Jun-hsiang

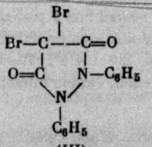
Whereas pyrazolones have been studied in considerable detail, the structurally similar pyrazolidine ring has received very little attention; thus, for example, the mechanism of the halogenation or thiocyanation of the latter remains obscure. As our investigations had shown, 1,2-diphenyl-3,5-dioxopyrazolidine (I) readily reacts with chlorine, bromine and thiocyanogen to form the corresponding monochloro, bromo and thiocyanato derivatives (II). The reaction goes both with cooling and at room temperature, without the use of catalysts, according to the scheme

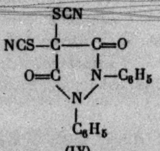

(I) (II)

where X = Cl, Br or CNS.

For the chlorination we used chlorine gas and chloroform as the solvent, while the bromination was run using bromine and again chloroform as the solvent (the bromination was run with cooling). The thiocyanation was run at 0-2° using thiocyanogen, obtained by the reaction of bromine with ammonium thiocyanate in methanol that had been saturated with ammonium bromide [1]. The high reactivity shown by the hydrogens at C_4 in the pyrazolidine ring, observed during halogenation and thiocyanation, permitted us to conclude that it is possible to halogenate (brominate) 1,2-diphenyl-3,5-dioxopyrazolidine (I) without the use of ultraviolet, as had recently been described in the literature [2].

Only the 4-monochloro derivative is formed when a chloroform solution of 1,2-diphenyl-3,5-dioxopyrazolidine is saturated with chlorine either in the cold or at chloroform boil, or when the chlorination is run in a melt (at 100-105°). In contrast to this, bromination using two moles of bromine yields the 4,4-dibromo derivative (III). The dithiocyanato derivative (IV) is also easily formed when the pyrazolidine is reacted with two moles of thiocyanogen.


(III)

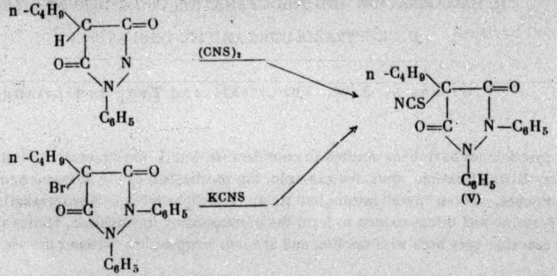

(IV)

In order to determine the effect of a substituent at C_4 on the entrance of a halogen or pseudohalogen (thiocyanogen) into the pyrazolidine molecule, we investigated the halogenation and thiocyanation of 4-n-butyl-1,2-

diphenyl-3,5-dioxopyrazolidine, i.e., when one of the hydrogens at C_4 was replaced; here it was established that the n-butyl radical is practically without influence on the mechanism of the reaction.

4-Chloro-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine was obtained under the same conditions used to chlorinate 1,2-diphenyl-3,5-dioxopyrazolidine; 4-bromo-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine was synthesized by the bromination of 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine in boiling chloroform.

4-Thiocyanato-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine (V) was obtained by two routes: a) by the thiocyanation of 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine, analogous to the thiocyanation of 1,2-diphenyl-3,5-dioxopyrazolidine, and b) the reaction of 4-bromo-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine with potassium thiocyanate in boiling alcohol.



Both in the case of 1,2-diphenyl-3,5-dioxopyrazolidine and its 4-n-butyl derivative it is the hydrogen of the methylene group that is replaced by chlorine, bromine or the thiocyanato radical during halogenation and thiocyanation; replacement of the hydrogens of the aromatic ring is less probable here. This follows from the fact that the chlorine, bromine or thiocyanato radical of the corresponding halo or thiocyanato pyrazolidines show easy exchange reaction. The same is also indicated by the fact that 1,2-diphenyl-3,5-dioxopyrazolidine and its 4-halo derivative are readily soluble in alkalies, whereas the 4,4-dihalo- or the 4-halo-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidines are insoluble in alkalies.

EXPERIMENTAL

1,2-Diphenyl-3,5-dioxopyrazolidine. To a solution of 4.6 g of sodium in 100 ml of anhydrous alcohol was added 32 g of malonic ester and 21.22 g of hydrazobenzene. The reaction mixture was boiled with constant stirring in a three-necked flask, fitted with a reflux condenser and calcium chloride tube, until a homogeneous mass was obtained. Then the reflux condenser was replaced by a descending condenser, and with constant stirring the alcohol was distilled off until the temperature of the reaction mixture reached 180-200°. The reaction mass after cooling was treated with 200 ml of water, the alkaline filtrate extracted with ether, and then it was acidified with dilute hydrochloric acid. The precipitate after washing with water and recrystallization from alcohol gave 45.4 g (90%) of a substance with m.p. 173.5°,-from its melting point and other properties corresponding to 1,2-diphenyl-3,5-dioxopyrazolidine, described in the literature [3].

4-Chloro-1,2-diphenyl-3,5-dioxopyrazolidine. Chlorine was passed for one hour into a solution of 1 g of 1,2-diphenyl-3,5-dioxopyrazolidine in 10 ml of chloroform at room temperature, and here a slight amount of exothermic heat was observed. The reaction product was poured into a porcelain dish, and the chloroform was evaporated in the air; the residue was a viscous yellow oil that soon crystallized. After recrystallization from benzene we obtained 1.02 g (90%) of a substance with m.p. 113-114.5°. The compound was obtained as white crystals, readily soluble in alkalies, chloroform, alcohol, ether, carbon tetrachloride and acetone, and insoluble in water and acids.

Found %: C 62.75, 63.08; H 3.60, 3.90; N 9.45, 9.66. $C_{15}H_{11}O_2N_2Cl$. Calculated %: C 62.83; H 3.84; N 9.77.

4-Bromo-1,2-diphenyl-3,5-dioxopyrazolidine. A solution of 4.7 g of bromine in 20 ml of chloroform was added gradually from a dropping funnel to a solution of 6 g of 1,2-diphenyl-3,5-dioxopyrazolidine in 50 ml of chloroform with cooling and constant stirring; here the separation of pale-yellow crystals was observed, which gradually went into solution. The solution was stirred for four hours, then washed with water until neutral, dried over fused sodium sulfate, the chloroform vacuum-distilled, the residue extracted with petroleum ether, and after removal of the solvent by vacuum-distillation we obtained 6.4 g of a substance with m.p. 50-55°, from its melting point and other properties corresponding to 4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine, described in the literature [2].

4-Thiocyanato-1,2-diphenyl-3,5-dioxopyrazolidine. A solution of 1.4 g of bromine in 25 ml of methanol, saturated with ammonium bromide, was added from a dropping funnel, with cooling and stirring, to a mixture of 1 g of 1,2-diphenyl-3,5-dioxopyrazolidine, 1.8 g of ammonium thiocyanate and 25 ml of methanol. After stirring for one hour the reaction mixture was filtered, the filtrate treated with 100 ml of water, and the obtained precipitate was suction-filtered, washed with water, and dried. We obtained 1.08 g (80%) of a substance which, after recrystallization from alcohol, had m.p. 175-180° (with decomp.). The compound was obtained as white, lustrous plates, soluble in water, methanol and ethanol, and insoluble in ether, chloroform and in acids; the compound is soluble in caustic alkalies.

Found %: C 62.24, 62.38; H 3.59, 3.67; N 13.67, 13.65. $C_{16}H_{11}O_2N_3S$. Calculated %: C 62.14; H 3.59; N 13.60.

4,4-Dibromo-1,2-diphenyl-3,5-dioxopyrazolidine. A solution of 5 g of bromine in 20 ml of chloroform was added, with heating on the water bath and constant stirring, to a solution of 3 g of 1,2-diphenyl-3,5-dioxopyrazolidine in 50 ml of chloroform. The reaction solution was stirred for one hour, then washed with water until neutral, dried over fused sodium sulfate, the chloroform evaporated in the air, and the residue recrystallized from alcohol; we obtained 3.2 g of a substance with m.p. 136-138° (65.04%).

Found %: C 44.29, 44.01; H 2.73, 2.44; N 6.74, 7.04. $C_{15}H_{10}O_2N_2Br_2$. Calculated %: C 43.90; H 2.44; N 6.83.

4,4-Dithiocyanato-1,2-diphenyl-3,5-dioxopyrazolidine. When the reaction was run the same as described for the preparation of 4-thiocyanato-1,2-diphenyl-3,5-dioxopyrazolidine, but with half the amount of 1,2-diphenyl-3,5-dioxopyrazolidine, we observed that only a small amount of precipitate separated when the filtrate was treated with 100 ml of water. Acidification of the filtrate with dilute hydrochloric acid gave a copious precipitate, which was soluble in water and in alcohol; recrystallization from 60° alcohol gave 1.14 g (80%) of crystals with m.p. 154-156°, insoluble in both acids and alkalies.

Found %: C 55.70, 56.17; H 3.09, 2.98; N 15.25, 14.76. $C_{17}H_{10}O_2N_4S_2$. Calculated %: C 55.74; H 2.73; N 15.30.

4-Chloro-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine. A stream of chlorine was passed for one hour into a solution of 1 g of 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine in 10 ml of chloroform at room temperature (here a slight evolution of heat was observed). The reaction mixture was poured into a porcelain dish, the chloroform allowed to evaporate spontaneously, and the residue recrystallized from alcohol to give 0.95 g (85%) of a substance with m.p. 100-101.5°. The compound was obtained as white crystals, soluble in alcohol, and insoluble in water, alkalies and acids.

Found %: C 66.43, 66.64; H 5.57, 5.41; N 8.16, 8.55. $C_{19}H_{19}O_2N_2Cl$. Calculated %: C 66.57; H 5.55; N 8.18.

4-Bromo-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine. A solution of 1.6 g of bromine in 10 ml of chloroform was added slowly in one hour, with constant stirring, to a solution of 3 g of 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine in 30 ml of chloroform at 60-70°. After washing with water, the chloroform layer was separated, dried over fused sodium sulfate, and the solvent allowed to evaporate in the air; recrystallization from alcohol gave 3.2 g (84%) of a substance with m.p. 116-118°, from its melting point and other properties corresponding to 4-bromo-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine, described in the literature [4].

4-Thiocyanato-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine. A solution of 1.2 g of bromine in 25 ml of methanol, saturated with ammonium bromide, was added in one hour and with constant stirring to a mixture of 2 g 2 g of 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine, 1.5 g of ammonium thiocyanate and 25 ml of methanol; here the 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine went into solution. The addition of 100 ml of water to the reaction mass gave an oily liquid that soon crystallized, and after recrystallization from alcohol we obtained

2.16 g (90%) of a substance with m.p. 105-106°. The compound was obtained as white lustrous plates, insoluble in water, alkalies and acids, and soluble in alcohol, ether and chloroform.

Found %: C 65.71, 65.44; H 5.80, 5.24; N 11.77, 11.62. $C_{20}H_{19}O_2N_3S$. Calculated %: C 65.75; H 5.21; N 11.51.

Study of the reaction of 4-bromo-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine with potassium thiocyanate. 4-Bromo-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine (1.5 g) was added gradually to a solution of 0.5 g of potassium thiocyanate in 20 ml of anhydrous alcohol; here a precipitate separated immediately. After refluxing for four hours the precipitate was filtered, washed with water and dried to give 1.4 g of a substance with m.p. 103-104°, from its melting point, analysis and other properties corresponding to 4-n-butyl-4-thiocyanato-1,2-diphenyl-3,5-dioxopyrazolidine, identical with that obtained earlier by the direct thiocyanation of 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine. The mixed melting point with an authentic specimen was not depressed.

SUMMARY

1. The reaction of halogens (chlorine, bromine), and also of a pseudohalogen (thiocyanogen), with 1,2-diphenyl-3,5-dioxopyrazolidine was investigated, in which connection the corresponding 4-chloro, 4-bromo and 4-thiocyanato derivatives of 1,2-diphenyl-3,5-dioxopyrazolidine were isolated.

2. It was shown that the reaction of a double amount of halogen or of pseudohalogen (thiocyanogen) with 1,2-diphenyl-3,5-dioxopyrazolidine yields the 4,4-dibromo and 4-4-dithiocyanato derivatives of 1,2-diphenyl-3,5-dioxopyrazolidine (we were unable to isolate 4,4-dichloro-1,2-diphenyl-3,5-dioxopyrazolidine).

3. It was found that the chlorination, bromination or thiocyanation of 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine yields the corresponding 4-chloro, 4-bromo and 4-thiocyanato derivatives of 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine.

4. It was found that 4-bromo-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine reacts with potassium thiocyanate to yield 4-thiocyanato-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine.

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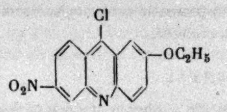
SYNTHESIS AND INVESTIGATION OF N-OXIDES OF HETEROCYCLIC COMPOUNDS

II. N-OXIDES OF ACRIDINE DERIVATIVES

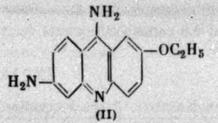
A.M. Khaletskii, V.G. Pesin and Chou Ch'ing

In a preceding communication, data were presented from the synthesis and study of certain properties of the N-oxides of morphine, tetrahydroisoquinoline, and quinoline derivatives [1]. In the present paper, data are presented relating to the properties of some N-oxides of the acridine series. The interest in such compounds arises in connection with their importance in medicine and as intermediate products in synthesis; moreover, the oxidation of acridine derivatives has received comparatively little study. Thus, acridine N-oxides can be obtained by reduction of acridone N-oxides and by oxidation of acridine [2].

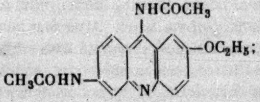
We studied the following acridine derivatives: 2-ethoxy-6-nitro-9-chloroacridine (I), 2-ethoxy-6,9-diaminoacridine (II), 2-ethoxy-6,9-di(acetylamino)acridine (III), 3,6-diaminoacridine (IV), and 3,6-di(acetylamino)acridine (V).


Cl
OC_2H_5
O_2N
N

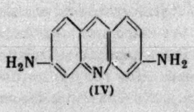
(I)


NH_2
OC_2H_5
H_2N
N

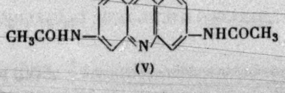
(II)


$NHCOCH_3$
OC_2H_5;
CH_3COHN
N

(III)

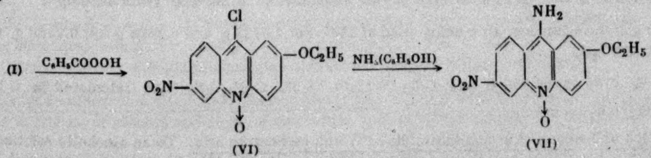


(IV)


CH_3COHN
$NHCOCH_3$
N

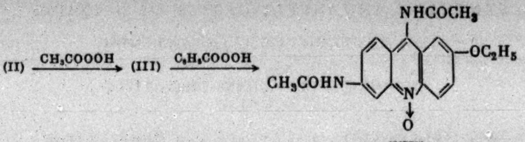
(V)

Oxidation of (I) with perbenzoic acid in chloroform gave an 89% yield of its N-oxide (VI), which, by interaction with gaseous ammonia (in phenol solution) was converted to the N-oxide of 2-ethoxy-6-nitro-9-aminoacridine (VII).


(I)
C_6H_5COOOH
Cl
OC_2H_5
O_2N
N
O
(VI)
$NH_3(C_6H_5OH)$
NH_2
OC_2H_5
O_2N
N
O
(VII)

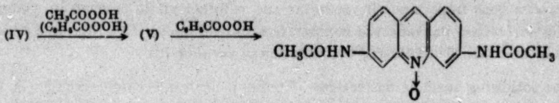
Thus, it was shown that the N-oxide group has no appreciable effect on the mobility of the chlorine; the chlorine in both (I) and (VI) readily enters into exchange reactions.

Upon oxidation of 2-ethoxy-6,9-diaminoacridine (II) with perbenzoic acid, no N-oxide was detected, and oxidation with peracetic acid (in the presence of acetic acid) and subsequent chromatization of the reaction products over aluminum oxide gave an 18.6% yield of 2-ethoxy-6,9-di(acetylamino)acridine (III); the latter was converted by oxidation with perbenzoic acid to the N-oxide of 2-ethoxy-6,9-di(acetylamino)acridine (VIII). Refluxing (VIII) with an aqueous-alcoholic solution of sodium hyposulfite gave (II).



(VIII)

3,6-Diaminoacridine (IV) behaved similarly with respect to peracetic and perbenzoic acids. Acylation occurred during the action of the latter acid on (IV), no N-oxide being detected under the conditions of the experiment. Oxidation of 3,6-di(acetylamino)acridine (V) with perbenzoic acid gave its N-oxide (IX).



(IX)

Thus, the peracids tested by us are not suitable for the direct conversion of aminoacridines to the corresponding N-oxides. When aminoacridines are oxidized with peracetic acid, acylation takes place first, and only then are the N-oxides of the corresponding acyl derivatives formed.

EXPERIMENTAL

N-Oxide of 2-ethoxy-6-nitro-9-chloroacridine (VI). To a solution of 1.6 g of 2-ethoxy-6-nitro-9-chloroacridine (I) in 400 ml of chloroform at 18-20° was added from a dropping funnel, with constant stirring, a chloroform solution (15 ml) of perbenzoic acid containing 1.065 g of the latter. After four hours, the solution was filtered, the chloroform was evaporated, and the red-colored residue was treated with a 5% solution of ammonia. The residue insoluble in the ammoniacal solution was filtered, washed with water, and dried at 50°; 1.5 g (89.28%) of material was obtained. After recrystallization from chloroform, bright-red crystals were obtained in the form of long needles with m.p. 204-206° (with decomp.).

Found %: C 56.51, 56.78; H 3.54, 3.56; N 9.13, 8.79. $C_{15}H_{11}O_4N_2Cl$. Calculated %: C 56.51; H 3.54; N 8.79.

N-Oxide of 2-ethoxy-6-nitro-9-aminoacridine (VII). 0.5 g of (VI) was dissolved in 1.25 g of molten phenol, and dry ammonia was passed into the solution at 100-105°; amination was continued until a thick mass was obtained. On treatment of the latter with alcohol, a dark-brown precipitate was formed which, after separation and washing with hot water, was dried at 60°; 0.35 g (74.2%) of material was obtained. Solution in alcohol and precipitation with water gave a dark-red powder which melted at 262-265° (with decomp.).

0.2542 g of the substance, after being dried at 120°, lost 0.0138 g, and 0.3562 g lost 0.0188 g, which corresponds to 5.43% H_2O.

Found %: C 56.40, 56.70; H 5.14, 4.73; N 13.00, 12.98. $C_{15}H_{13}O_4N_3 \cdot H_2O$. Calculated %: C 56.78; H 4.73; N 13.25.

Oxidation of 2-ethoxy-6,9-diaminoacridine (II) with perbenzoic acid. To an alcoholic solution of perbenzoic acid (7.5 g in 42 ml of alcohol), cooled to 10°, was gradually added, with stirring, 75 ml of an alcoholic solution of (II) containing 9.8 g of the latter. The resulting precipitate was filtered, washed with sodium hydroxide solution, and dried at 100°; m.p. 113-118°. A mixed sample with known 2-ethoxy-6,9-diaminoacridine showed no melting point depression.

Oxidation of 2-ethoxy-6,9-diaminoacridine (II) with peracetic acid. 2 g of 2-ethoxy-6,9-diaminoacridine was dissolved in 2 ml of 98% acetic acid; the solution was diluted with 200 ml of water, and to this solution was gradually added, with continuous stirring, 13 ml of peracetic acid in acetic acid containing 0.78 g of peracetic acid. After the dark-red solution had been stirred for ten minutes, it was neutralized with 10% sodium hydroxide solution, and the resulting precipitate was filtered, washed with water, and dried; 1.95 g was obtained. An alcoholic solution of the precipitate was passed through an aluminum oxide column (activated by drying at 300° for three hours). After development with alcohol, three zones were observed on the aluminum oxide. The lower part was pale yellow, the middle was brown, and the upper was yellow-brown.

An alcoholic solution of the material contained in the lower part* of the column was evaporated to dryness at 60°, resulting in the formation of lustrous, yellowish-brown needles; the 0.5 g of material (after recrystallization from a 1:1 mixture of alcohol and ether) corresponded to a yield of 18.6% based on the 2-ethoxy-6,9-diaminoacridine; the material did not melt when heated to 270°.

Found %: C 59.95, 60.10; H 6.36, 6.52; N 12.00, 12.27. $C_{14}H_{19}O_3N_3 \cdot 1.5H_2O$. Calculated %: C 60.00; H 6.47; N 12.36.

On the basis of the analytical data, the substance was the acetic acid salt of 2-ethoxy-6,9-diaminoacridine. This compound was readily soluble in water, and neutralization of the solution with a 10% solution of sodium hydroxide caused separation of a yellow precipitate. A mixed sample with known 2-ethoxy-6,9-diaminoacridine showed no depression of the melting point.

An alcoholic solution of the material from the center of the column was evaporated, and the residue was dried at 60° to give a yellowish-brown material. 2-Ethoxy-6,9-diaminoacridine and its acetate were separated from the material.

Evaporation of an alcoholic solution of the material contained in the lower part* of the column left a red residue, which, after recrystallization from alcohol, decomposed without melting at 235°; it did not give a cherry-red color when acted on by sodium nitrite in the presence of hydrochloric acid, and its nature remains unclear.

2-Ethoxy-6,9-di(acetylamino)acridine (III). 20 g of 2-ethoxy-6,9-diaminoacridine was acylated with 16 g of acetic anhydride by heating to 100° until all amino groups were substituted with acetyl radicals (i.e., to a negative reaction with sodium nitrite). On dilution of the solution with 0.5 liter of water, 11.9 g of a yellow material separated, and an additional 9.5 g was recovered from the mother liquor; a total of 22.4 g (88.3%) of material was obtained, m.p. 290-292°. Recrystallization from a mixture of pyridine and water gave yellow needles with an m.p. of 296-297° (with decomp.), which were readily soluble in pyridine and less soluble in alcohol, benzene, chloroform, dichloroethane, and other organic solvents.

Found %: C 61.30, 60.94; H 6.35, 6.35; N 11.36, 11.26. $C_{19}H_{19}O_3N_3 \cdot 2H_2O$. Calculated %: C 61.13; H 6.16; N 11.26.

When dried at 120°, 0.6159 g and 0.4580 g of the substance lost, respectively, 0.0588 g and 0.0432 g, which corresponds to 2 moles of water.

Found, after saponification with 0.1 N alcoholic potassium hydroxide, %: CH_3COOH 31.1, 31.4. $C_{19}H_{19}O_3N_3 \cdot 2H_2O$. Calculated %: CH_3COOH 31.33.

When the 2-ethoxy-6,9-di(acetylamino)acridine was refluxed with concentrated sulfuric acid, an odor of ethyl acetate developed, and simultaneously a yellow precipitate, with an m.p. of 110°, separated. A mixed sample with known 2-ethoxy-6,9-diaminoacridine showed no depression of the melting point.

N-Oxide of 2-ethoxy-6,9-di(acetylamino)acridine (VIII). 1 g of 2-ethoxy-6,9-di-(acetylamino)acridine was dissolved in 300 ml of alcohol and 50 ml of chloroform, and to the solution was added, with constant stirring,

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*There is an inconsistency here. Another paragraph refers to the lower part of the column, also. One of the two probably is meant to refer to the upper part of the column – Editor's note.

8 ml of a chloroform solution of perbenzoic acid containing 0.56 g of the latter. After three hours, the solvent was evaporated (in air), and, after the yellowish-brown residue had been washed with ether, 0.95 g (90.6%) of material was obtained, which, after recrystallization from alcohol, melted at 247-248° (with decomp.) and which was in the form of yellow needles.

When dried at 120°, 0.2402 g and 0.2282 g of the substance lost, respectively, 0.0173 g and 0.0165 g, which corresponds to 1.5 molecules of water.

Found %: C 59.81, 60.24; H 6.07, 6.05; N 11.40, 11.18. $C_{19}H_{19}O_4N_3 \cdot 1.5H_2O$. Calculated %: C 60.00; H 5.79; N 11.05.

Oxidation of 3,6-diaminoacridine with perbenzoic acid. 1 g of (IV) was dissolved in 100 ml of chloroform and 5 ml of alcohol, and to the solution, which was at 15°, was added 14 ml of a chloroform solution of perbenzoic acid which contained 0.84 g of perbenzoic acid. The brown precipitate was filtered, and neutralized with a 10% solution of sodium hydroxide. It melted at 264-267° after being washed with water and dried. A mixed sample with known 3,6-diaminoacridine showed no depression of the melting point.

Oxidation of 3,6-diaminoacridine with peracetic acid. 2 g of (IV) was dissolved in 2 ml of 98% acetic acid, and the solution was diluted with 250 ml of water and oxidized with 16 ml of an acetic acid solution of peracetic acid containing 0.96 g of the latter. On neutralization with a 10% solution of ammonia, a fine, dark-brown precipitate separated, which was filtered and dried. Similarly to the case of the oxidation of 2-ethoxy-6,9-diaminoacridine with peracetic acid, the residue was a mixture of products of the oxidation of 3,6-diaminoacridine.

3,6-Diacetylaminoacridine [3]. A mixture of 2 g of 3,6-diacetylaminoacridine, 200 ml of chloroform, 1000 ml of alcohol was subjected to oxidation with 1.2 g of perbenzoic acid (in chloroform). After four hours, the solvent was removed by evaporation, and the residue was washed with ether and dried at 100°; 1.9 g of material was obtained, m.p. 175-188°. Solution in alcohol and precipitation with water gave 0.2 g (9.16%) of a substance with an m.p. of 236° (with decomp.); this was a yellowish-brown powder, soluble in alcohol and insoluble in water.

Found %: C 60.28, 60.71; H 5.73, 5.59; N 12.56, 12.20. $C_{17}H_{15}O_3N_3 \cdot 1.5H_2O$. Calculated %: C 60.71; H 5.36; N 12.50.

When dried at 120°, 0.2318 g and 0.1946 g of the substance lost, respectively, 0.0182 g and 0.0146 g, which corresponds to 1.5 molecules of water.

SUMMARY

The behavior of oxidizing agents (peracetic and perbenzoic acids) toward certain acridine derivatives was investigated. It was found that, on oxidation with peracetic acid, 2-ethoxy-6,9-diamino- and 3,6-diaminoacridine are first acetylated, and then form the N-oxides; oxidation of 2-ethoxy-6-nitro-9-chloroacridine forms the N-oxide in the normal manner, and replacement of the chlorine at C_9 by an amino group is not hindered by the N-oxide group.

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[1] A.M. Khaletskii, V.G. Pesin and Chou Ch'ing, J. Gen. Chem. 28, 2348 (1958).*

[2] A. Albert, The Acridines (London, 1948).

[3] K. Lemstedt and H. Klee, Ber. 69, 1155 (1936).

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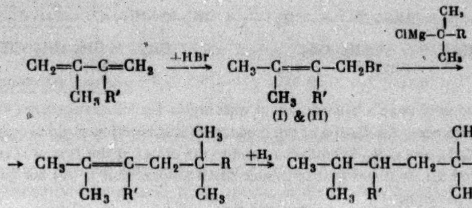
* Original Russian pagination. See C.B. translation.

SYNTHESIS OF HYDROCARBONS

LXVII. C_{12} HYDROCARBONS WITH ONE AND TWO QUATERNARY CARBON ATOMS

R.Ia. Levina, P.A. Kaikaris and P.A. Gembitskii

A previous communication [1] described the synthesis of ethylenic (and from them, by hydrogenation – paraffinic) C_9-C_{11} hydrocarbons with single quaternary carbon atoms by the interaction of tert-alkylmagnesium chlorides (tert-butyl- and tert-amylmagnesium chlorides) with primary hydrohalides of isoprene [haloolefins] and 2,3-dimethyl-1,3-butadiene.



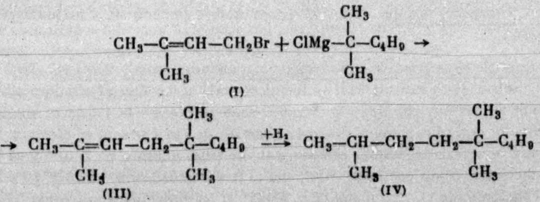
$$CH_2{=}\underset{CH_3}{C}{-}\underset{R'}{C}{=}CH_2 \xrightarrow{+HBr} CH_3{-}\underset{CH_3}{C}{=}\underset{R'}{C}{-}CH_2Br \xrightarrow{ClMg-\overset{CH_3}{\underset{CH_3}{C}}-R}$$

(I) & (II)

$$\rightarrow CH_3{-}\underset{CH_3}{C}{=}\underset{R'}{C}{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}R \xrightarrow{+H_2} CH_3{-}\underset{CH_3}{CH}{-}\underset{R'}{CH}{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}R$$

$R' = H$ (I), CH_3 (II);
$R = CH_3$, C_2H_5.

In the present work, the primary hydrobromide of isoprene [1-bromo-3-methyl-2-butene] (I) was used for the synthesis of ethylenic and paraffinic hydrocarbons having the composition $C_{12}H_{24}$ and $C_{12}H_{26}$. The interaction of isoprene hydrobromide with 2-chloromagnesium-2-methylhexane [2-methylhexylmagnesium bromide] gave an alkene with one quaternary carbon atom – 2,5,5-trimethyl-2-nonene (III), and hydrogenation of the alkene gave 2,5,5-trimethylnonane (IV).



$$\underset{(I)}{CH_3{-}\underset{CH_3}{C}{=}CH{-}CH_2Br} + ClMg{-}\overset{CH_3}{\underset{CH_3}{C}}{-}C_4H_9 \rightarrow$$

$$\rightarrow \underset{(III)}{CH_3{-}\underset{CH_3}{C}{=}CH{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}C_4H_9} \xrightarrow{+H_2} \underset{(IV)}{CH_3{-}\underset{CH_3}{CH}{-}CH_2{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}C_4H_9}$$

The reaction of isoprene hydrobromide with an organomagnesium compound isomeric with 2-chloro-2-methylhexane and having a more branched structure – 3-chloromagnesium-2,2,3-trimethylbutane [1,1,2,2-tetramethylpropylmagnesium chloride] (triptylmagnesium chloride*) – gave a $C_{12}H_{24}$ ethylenic hydrocarbon (V) with two adjacent quaternary carbon atoms – 2,2,3,3,6-pentamethyl-5-heptene – and hydrogenation of this compound gave 2,2,3,3,6-pentamethylheptane (VI).

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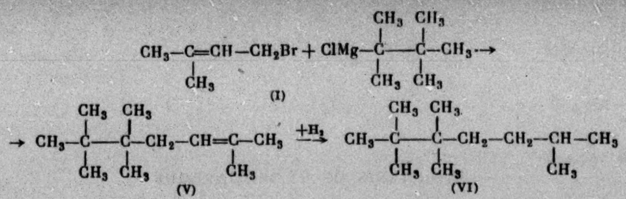
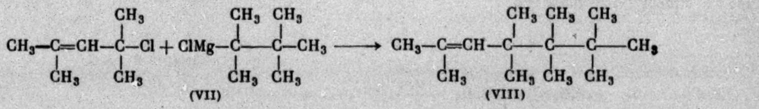
*A.D. Petrov and co-workers[2] have described the synthesis of alkenes (in yields of 3 and 6.5%) by the interaction of triptyl chloride with magnesium and the simplest allylic chlorides – allyl and methallyl chloride. Similar reactions have also been described by these authors for other chlorides of the triptyl type.



$$CH_3-\overset{CH_3}{\underset{}{C}}=CH-CH_2Br + ClMg-C(CH_3)_2-C(CH_3)_2-CH_3 \rightarrow CH_3-C(CH_3)_2-C(CH_3)_2-CH_2-CH=C(CH_3)-CH_3 \xrightarrow{+H_2} CH_3-C(CH_3)_2-C(CH_3)_2-CH_2-CH_2-CH(CH_3)-CH_3$$

(I) (V) (VI)

These isomeric $C_{12}H_{24}$ alkenes and the isomeric $C_{12}H_{26}$ alkanes having one and two quaternary carbon atoms have not been described in the literature. The yields of both isomeric alkenes (III and V) were only 8 and 7%, calculated on the organomagnesium compound formed (the content of which in the ether solution was determined by titration). The low yields of alkenes is explained by the occurrence of numerous side processes which proceeded during the reactions between the diene hydrohalides and the tert-alkylmagnesium chlorides [3]. We made a further attempt to carry out the synthesis of a $C_{14}H_{28}$ hydrocarbon having three neighboring quaternary carbon atoms (VIII) by introducing triptylmagnesium chloride into a reaction with a tertiary allyl chloride – the hydrochloride of 2,4-dimethyl-1,3-pentadiene (VII).*



$$CH_3-C(CH_3)=CH-C(CH_3)_2-Cl + ClMg-C(CH_3)_2-C(CH_3)_2-CH_3 \longrightarrow CH_3-C(CH_3)=CH-C(CH_3)_2-C(CH_3)_2-C(CH_3)_2-CH_3$$

(VII) (VIII)

However, the attempt to synthesize a hydrocarbon of such highly branched structure (VIII) was unsuccessful, apparently owing to steric hindrance; distillation of the products of this reaction yielded only fractions corresponding in boiling points to C_7H_{12} and C_7H_{14} hydrocarbons and to the dimer of the first of these. A $C_{14}H_{28}$ hydrocarbon either was not formed at all, or it was formed in such small amount that it was not possible to separate it by distillation of the reaction products.

EXPERIMENTAL

The tertiary chlorides – 2-chloro-2-methylhexane and 3-chloro-2,2,3-trimethylbutane (triptyl chloride) – were prepared from the corresponding tertiary alcohols, 2-methyl-2-hexanol (b.p. 54-54.5° at 12 mm; literature value [5] 138-139° at 742 mm) and 2,2,3-trimethyl-3-butanol (triptanol) (m.p. 16°; literature value [6], m.p. 16°), by agitation with a two-fold amount of concentrated hydrochloric acid saturated at 0° with hydrogen chloride. The resulting chlorides (yield, 90%) were washed with water and dried. 2-Chloro-2-methylhexane: b.p. 36-37° at 14 mm, n_D^{20} 1.4212, d_4^{20} 0.8669. Literature data [5]: b.p. 127-128° at 753 mm, n_D^{20} 1.4193, d_4^{20} 0.8669. 3-Chloro-2,2,3-trimethylbutane: m.p. 130° (from methyl alcohol; in a sealed capillary). Literature data [6]: m.p. 128-134°.

Interaction of isoprene hydrobromide with 2-chloromagnesium-2-methylhexane. To 3 g-atoms of magnesium (preliminarily activated by heating with an iodine crystal) in 0.5 liter of absolute ether was slowly added a solution of 3 moles of the tertiary chloride – 2-chloro-2-methylhexane – in 1 liter of absolute ether. The resulting ethereal solution of organomagnesium compound was filtered in a stream of nitrogen from the unreacted magnesium (the content of organomagnesium compound in the ether solution, as determined by titration [7], was 56% of theoretical), the solution was cooled to −40°, and to it was added, with stirring, an ethereal solution (1:1) of primary isoprene hydrobromide [1] (1.7 mole; b.p. 58-62° at 56 mm; literature value [8]: b.p. 60-65° at 63 mm).

The reaction mixture was heated and stirred for several hours, and was decomposed by pouring onto a mixture of ice and acetic acid. After the usual treatment of the ether extracts and distillation of the ether and low-boiling (to 140°) fractions containing C_7H_{14} hydrocarbons and unreacted unsaturated tertiary chloride, the residue was distilled from polymers, refluxed over sodium to a negative reaction for halide, and distilled in a column. After two fractional distillations, 21 g of 2,5,5-trimethyl-2-nonene (8% calculated on the organomagnesium compound formed) was isolated; the nonene had the following constants:

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*As we have shown previously [3, 4], the hydrochloride and hydrobromide of 2,4-dimethyl-1,3-pentadiene enter into a Grignard-Wurtz reaction with tert-alkylmagnesium chlorides (of less branched structure than triptylmagnesium chloride) forming hydrocarbons with two neighboring quaternary carbon atoms.

B.p. 64.5-65° (4 mm), n_D^{20} 1.4421, d_4^{20} 0.7802; MR_D 57.10; calc. 57.15 (57.23[*]).

Found %: C 85.62, 85.73; H 14.42, 14.33. $C_{12}H_{24}$. Calculated %: C 85.63; H 14.37.

Interaction of isoprene hydrobromide with 3-chloromagnesium-2,2,3-trimethylbutane (triptylmagnesium chloride). The reaction was carried out by the method described above. The content of organomagnesium compound in the ether solution was 50%. Distillation of the reaction products gave a hydrocarbon fraction boiling at 150-200°, which was refluxed with sodium to the complete removal of halogen compounds and distilled over sodium in a column. Two fractional distillations gave 18 g of 2,2,3,3,6-pentamethyl-5-heptene (7% calculated on the organomagnesium compound formed) with the following constants:

B.p. 195.5° (750 mm), n_D^{20} 1.4493, d_4^{20} 0.7950, MR_D 56.82; calc. 57.15 (56.83).

Found %: C 85.62, 85.82; H 14.48, 14.41. $C_{12}H_{24}$. Calculated %: C 85.63; H 14.37.

Hydrogenation of both isomeric $C_{12}H_{24}$ alkenes was carried out over nickel on aluminum oxide at 170-180°. The resulting alkanes had the following constants after distillation in a column:

2,5,5-Trimethylnonane – b.p. 59° (5 mm), n_D^{20} 1.4236, d_4^{20} 0.7550; MR_D 57.50; calc. 57.62 (57.60).

Found %: C 84.60, 84.72; H 15.43, 15.33. $C_{12}H_{26}$. Calculated %: C 84.62; H 15.38.

2,2,3,3,6-Pentamethylheptane – b.p. 187.5-188° (745 mm), n_D^{20} 1.4345, d_4^{20} 0.7772, MR_D 57.15; calc. 57.62 (57.20).

Found %: C 84.68, 84.82; H 15.42, 15.19. $C_{12}H_{26}$. Calculated %: C 84.62; H 15.38.

The Raman spectra of these alkenes had lines at, respectively, 1664 cm^{-1} and 1668 cm^{-1}, which confirmed their structure as trisubstituted ethylenes. In the spectra of the alkanes, intense lines were present in the regions of 671, 926, and 1240 cm^{-1}, which are characteristic of highly branched hydrocarbon chains containing quaternary carbon atoms [10].

Interaction of the hydrochloride of 2,4-dimethyl-1,3-pentadiene (2-chloro-2,4-dimethyl-3-pentene) with triptylmagnesium chloride. The hydrochlorination of 2,4-dimethyl-1,3-pentadiene and the reaction of the resulting hydrochloride (1.7 moles) with triptylmagnesium chloride (from 3 moles of triptyl chloride and 3 g-atoms of magnesium) were carried out by the method described previously [3] (for the reaction between the same hydrochloride and other tert-alkylmagnesium chlorides). During the first distillation of the reaction products, fractions were collected which boiled in the ranges of 80-120° (containing C_7H_{12} and C_7H_{14} hydrocarbons), 120-180° (consisting mainly of unreacted triptyl chloride), and 215-250°. The fraction boiling at 215-250° was refluxed over sodium (to the complete removal of halogen), and was then distilled in a column to give 38 g (12%) of the dimer of 2,4-dimethyl-1,3-pentadiene [11] with a b.p. of 90° at 10 mm (218-220° at 760 mm) and n_D^{20} 1.4800; several grams of a higher-boiling fraction (90-105° at 10 mm, 220-235° at 760 mm) was also obtained, but this fraction was not investigated further.

SUMMARY

1. Previously undescribed $C_{12}H_{24}$ alkenes with one and two quaternary carbon atoms, 2,5,5-trimethyl-2-nonene and 2,2,3,3,6-pentamethyl-5-heptene, were synthesized by the interaction of isoprene hydrobromide with the tert-alkylmagnesium chlorides 2-chloromagnesium-2-methylhexane and 3-chloromagnesium-2,2,3-trimethylbutane (triptylmagnesium chloride).

2. Hydrogenation of these alkenes gave 2,5,5-trimethylnonane and 2,2,3,3,6-pentamethylheptane, which also have not been described previously.

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[*] In parentheses (here and subsequently) is given MR_D calculated by the additive scheme of V.M. Tatevskii [9], which takes into account the subtypes of chemical bonds.

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*Original Russian pagination. See C.B. translation.

**As in Russian. (Probably as yet unpublished.) See forthcoming C.B. translation.

INTERACTION OF γ-CHLOROPROPYLSILANE CHLORIDES WITH AROMATIC COMPOUNDS BY FRIEDEL-CRAFTS REACTION

E.A. Chernyshev, M.E. Dolgaia and Iu.P. Egorov

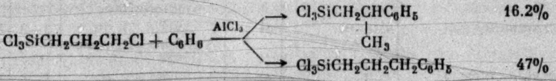
In preceding communications [1], we have described the interaction of various α- and β-chloroalkylsilane chlorides, obtained from methyl- and ethylchlorosilanes, with aromatic compounds in the presence of $AlCl_3$ or metallic aluminum. It was shown that β-chloroalkylsilane chlorides are considerably more active in this reaction than are α-chloroalkylsilane chlorides and also that aromatic compounds with the aromatic ring in the β-position are obtained quantitatively from α-chloroethyltrichlorosilane and partially from β-chloroethylethyldichlorosilane.

Continuing the investigation of the dependence of the reactivity of chloroalkylsilane chlorides on the position of the C−Cl bond relative to the silicon atom, in the present work we studied the interaction of β- and γ-chloropropyltrichlorosilanes and of β- and γ-chloropropylmethyldichlorosilanes with various aromatic compounds in the presence of $AlCl_3$ or of Al.

Both β-chloropropyltrichlorosilane and β-chloropropylmethyldichlorosilane react vigorously with benzene, toluene, and chlorobenzene to give the corresponding derivatives in yields of 40-60%. The reaction requires 10-15 hours at room temperature and 2-3 hours at 60-70°. In the case of diphenyl, diphenyl oxide, and naphthalene, only metallic aluminum was used as the catalyst in order to decrease tar formation. The yields of products in these cases were somewhat lower, but still comprised 20-40%. γ-Chloropropyltrichlorosilane and γ-chloropropylmethyldichlorosilane reacted just as vigorously as the corresponding β-isomers, and the yields of silicoalkylation products in this case, with few exceptions, were no lower.

Thus, even though the α-chloroalkylsilane chlorides have very low reactivity in comparison to the β-isomers, the reactivity of the γ-chloroalkylsilane chlorides is no less than the β-chlorides.

It might be expected that the γ-chlorides or the γ-carbonium ions, which are formed in the course of the reaction, would isomerize with the formation of the β-isomers. Precise fractionation showed that two substances corresponding to the β- and γ-isomers in a ratio of 1:2.9 actually are formed from γ-chloropropyltrichlorosilane and benzene. Only one substance is formed during the reaction of γ-chloropropylmethyldichlorosilane with benzene. All three compounds were methylated, and a comparison of their spectra showed that only the γ-isomer is formed in the second case.



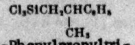
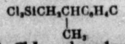
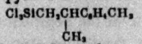
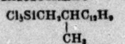
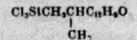
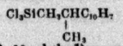
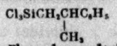
$$Cl_3SiCH_2CH_2CH_2Cl + C_6H_6 \xrightarrow{AlCl_3} \begin{cases} Cl_3SiCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HC_6H_5 & 16.2\% \\ Cl_3SiCH_2CH_2CH_2C_6H_5 & 47\% \end{cases}$$

$$CH_3SiCl_2CH_2CH_2CH_2Cl + C_6H_6 \xrightarrow{AlCl_3} Cl_3SiCH_2CH_2CH_2C_5H_6 \qquad 34\%$$

It is evident that γ-chloropropylmethyldichlorosilane is more reactive than γ-chloropropyltrichlorosilane in Friedel-Crafts reactions and that it enters into reactions with aromatic compounds without undergoing isomerization.

In order to establish the ratio of ortho-, meta-, and para-isomers in the silicoalkylation products of toluene, we carried out an analysis of the spectra (Raman spectra) of $(CH_3)_3SiCH_2CH_2CH_2C_6H_4CH_3$ and $(CH_3)_3SiCH_2CH(CH_3)$-$C_6H_4CH_3$. Since the spectra were identical, we present only the spectrum of the first substance:

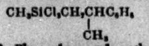
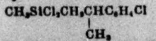
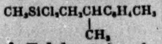
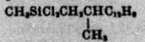
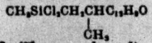
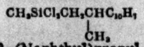
TABLE 1

Silicoalkylating agent	Aromatic compound	Catalyst	Compound obtained	Reaction time (hours)	Yield (in %) based on original chloride	Boiling point (pressure in mm)
$Cl_3SiCHClCH_2CH_3$	C_6H_6	Al	$Cl_3SiC_3H_6C_6H_5$ Phenylpropyltrichlorosilane	2—3	18.0	100° (6)
			$[Cl_3SiC_3H_6]_2C_6H_4$ Bis(trichlorosilylpropyl)benzene	2—3	14.4	172—173 (6)
$Cl_3SiCH_2CHClCH_3$	C_6H_6	$AlCl_3$	 $Cl_3SiCH_2\underset{\substack{\mid\\ CH_3}}{CH}C_6H_5$ β-Phenylpropyltrichlorosilane	22	53.25	101—102 (6)
$Cl_3SiCH_2CHClCH_3$	C_6H_5Cl	$AlCl_3$	 $Cl_3SiCH_2\underset{\substack{\mid\\ CH_3}}{CH}C_6H_4C$ β-Chlorophenylpropyltrichlorosilane	8	58.0	135—136 (8.5)
$Cl_3SiCH_2CHClCH_3$	$C_6H_5CH_3$	$AlCl_3$	 $Cl_3SiCH_2\underset{\substack{\mid\\ CH_3}}{CH}C_6H_4CH_3$ β-Tolylpropyltrichlorosilane	7—8	57.7	122.5 (9)
$Cl_3SiCH_2CHClCH_3$	$C_{12}H_{10}$	Al	 $Cl_3SiCH_2\underset{\substack{\mid\\ CH_3}}{CH}C_{12}H_9$ β-Xenylpropyltrichlorosilane	5—6	22.8	188—189 (6.5)
$Cl_3SiCH_2CHClCH_3$	$C_{12}H_{10}O$	Al	 $Cl_3SiCH_2\underset{\substack{\mid\\ CH_3}}{CH}C_{12}H_9O$ β-(p-Phenoxyphenyl)propyltrichlorosilane	1.5—2	42	183.5—185 (6)
$Cl_3SiCH_2CHClCH_3$	$C_{10}H_8$	Al	 $Cl_3SiCH_2\underset{\substack{\mid\\ CH_3}}{CH}C_{10}H_7$ (β-Naphthyl)propyltrichlorosilane	1.5—2	29.4	172 (8)
$Cl_3SiCH_2CH_2CH_2Cl$	C_6H_6	$AlCl_3$	 $Cl_3SiCH_2\underset{\substack{\mid\\ CH_3}}{CH}C_6H_5$ β-Phenylpropyltrichlorosilane	25—30	16.2	116—117 (10)
			$Cl_3SiCH_2CH_2CH_2C_6H_5$ γ-Phenylpropyltrichlorosilane	25—30	47.0	120 (10)
$Cl_3SiCH_2CH_2CH_2Cl$	C_6H_5Cl	$AlCl_3$	$Cl_3SiC_3H_6C_6H_4Cl$ Chlorophenylpropyltrichlorosilane	2—3	73	135 (5)
$Cl_3SiCH_2CH_2CH_2Cl$	$C_6H_5CH_3$	Al	$Cl_3SiC_3H_6C_6H_4CH_3$ Tolylpropyltrichlorosilane	2—3	34	126.5—127 (4)
$Cl_3SiCH_2CH_2CH_2Cl$	$C_{12}H_{10}$	Al	$Cl_3SiC_3H_6C_{12}H_9$ Xenylpropyltrichlorosilane	5—6	44.8	193—194 (6.5)

n_D^{20}	d_4^{20}	MR_D		Found (in %)				Empirical formula	Calculated (in %)			
		found	calc.	C	H	Si	Cl		C	H	Si	Cl
1.5155	1.2301	62.16	62.67	42.42, 42.68	4.43, 4.54	10.69, 10.81	40.90, 41.01	$C_9H_{11}SiCl_3$	42.61	4.33	11.06	42.00
1.5200	1.3156	99.59	98.97	33.73, 33.81	3.83, 3.84	12.54, 12.27	48.67, 48.42	$C_{12}H_{16}Si_2Cl_6$	33.57	3.73	13.04	49.66
1.5155	1.2260	62.37	62.67	42.80, 42.72	4.69, 4.48	10.51, 10.75	40.93, 41.13	$C_9H_{11}SiCl_3$	42.62	4.37	11.06	41.95
1.5300	1.3189	67.42	67.51	37.96, 37.65	3.40, 3.28	10.40, 10.44	48.16, 48.60	$C_9H_{10}SiCl_4$	37.52	3.52	9.74	49.22
1.5190	1.2002	67.70	67.30	44.71, 44.76	4.93, 4.79	10.59, 10.27	38.99, 38.59	$C_{10}H_{13}SiCl_3$	44.97	4.89	10.46	39.68
1.5765	1.2342	88.37	86.91	54.84, 54.86	4.63, 4.36	8.37, 8.50	31.84, 31.52	$C_{15}H_{15}SiCl_3$	54.65	4.55	8.50	32.30
1.5562	1.2471	89.15	88.68	52.41, 52.62	4.37, 4.38	8.45, 7.90	30.33, 30.48	$C_{15}H_{15}OSiCl_3$	52.12	4.34	8.10	30.79
1.5812	1.2617	80.19	78.12	51.90, 51.73	4.61, 4.78	8.13, 9.14	33.65, 33.22	$C_{13}H_{13}SiCl_3$	51.45	4.28	9.23	35.04
1.5159	1.2260	62.93	62.67	42.74, 42.94	4.48, 4.61	11.10, 11.12	40.68, 40.63	$C_9H_{11}SiCl_3$	42.62	4.37	11.06	40.95
1.5150	1.2248	62.38	62.67	42.68, 42.78	4.47, 4.62	11.20, 11.15	40.54, 40.69	$C_9H_{11}SiCl_3$	42.62	4.37	11.06	40.95
1.5292	1.3140	67.57	67.51	37.92, 37.88	3.59, 3.56	9.43, 9.71	48.22, 48.04	$C_9H_{10}SiCl_4$	37.52	3.52	9.74	49.22
1.5145	1.1988	67.19	67.30	45.13, 45.10	5.15, 5.13	10.43, 10.77	39.48, 39.53	$C_{10}H_{13}SiCl_3$	44.97	4.89	10.46	39.68
1.5768	1.2313	88.61	86.91	54.69, 54.60	5.13, 4.91	7.40, 7.68	31.13, 31.53	$C_{15}H_{15}SiCl_3$	54.65	4.55	8.50	32.30

(continued)

TABLE 1 (continued)

Silicoalkylating agent	Aromatic compound	Catalyst	Compound obtained	Reaction time (hours)	Yield (in %) based on original chloride	Boiling point (pressure in mm)
$Cl_3SiCH_2CH_2CH_2Cl$	$C_{12}H_{10}O$	Al	$Cl_3SiC_3H_6C_{12}H_9O$ Phenoxyphenylpropyltrichlorosilane	5—6	48.3	196—197 (8)
$Cl_3SiCH_2CH_2CH_2Cl$	$C_{10}H_8$	Al	$Cl_3SiC_3H_6C_{10}H_7$ Naphthylpropyltrichlorosilane	2—3	6.3	172—174 (7.5)
$CH_3SiCl_2CH_2CHClCH_3$	C_6H_6	Al	 $CH_3SiCl_2CH_2\underset{\underset{CH_3}{\mid}}{C}HC_6H_5$ β-Phenylpropylmethyldichlorosilane	3—4	43.5	99 (6)
$CH_3SiCl_2CH_2CHClCH_3$	C_6H_5Cl	Al	 $CH_3SiCl_2CH_2\underset{\underset{CH_3}{\mid}}{C}HC_6H_4Cl$ β-Chlorophenylpropylmethyldichlorosilane	3—4	40.0	126—127 (6)
$CH_3SiCl_2CH_2CHClCH_3$	$C_6H_5CH_3$	Al	 $CH_3SiCl_2CH_2\underset{\underset{CH_3}{\mid}}{C}HC_6H_4CH_3$ β-Tolylpropylmethyldichlorosilane	3—4	40.0	111 (6)
$CH_3SiCl_2CH_2CHClCH_3$	$C_{12}H_{10}$	Al	 $CH_3SiCl_2CH_2\underset{\underset{CH_3}{\mid}}{C}HC_{12}H_9$ β-Xenylpropylmethyldichlorosilane	6—8	16	187—190 (6.5)
$CH_3SiCl_2CH_2CHClCH_3$	$C_{12}H_{10}O$	Al	 $CH_3SiCl_2CH_2\underset{\underset{CH_3}{\mid}}{C}HC_{12}H_9O$ β-(Phenoxyphenyl)-propylmethyldichlorosilane	6—8	26.6	180—184 (7)
$CH_3SiCl_2CH_2CHClCH_3$	$C_{10}H_8$	Al	 $CH_3SiCl_2CH_2\underset{\underset{CH_3}{\mid}}{C}HC_{10}H_7$ β-(Naphthyl)propylmethyldichlorosilane	2—3	26	171 (6)
$CH_3SiCl_2CH_2CH_2CH_2Cl$	C_6H_6	$AlCl_3$	$CH_3SiCl_2CH_2CH_2CH_2C_6H_5$ γ-Phenylpropylmethyldichlorosilane	8—10	34.0	114—115 (6)
$CH_3SiCl_2CH_2CH_2CH_2Cl$	C_6H_5Cl	Al	$CH_3SiCl_2CH_2CH_2CH_2C_6H_4Cl$ γ-Chlorophenylpropylmethyldichlorosilane	4—5	43.6	130—131 (6.5)
$CH_3SiCl_2CH_2CH_2CH_2Cl$	$C_6H_5CH_3$	Al	$CH_3SiCl_2CH_2CH_2CH_2C_6H_4CH_3$ γ-Tolylpropylmethyldichlorosilane	6—8	60.8	123—125 (7)
$CH_3SiCl_2CH_2CH_2CH_2Cl$	$C_{11}H_8$	Al	$CH_3SiCl_2CH_2CH_2CH_2C_{10}H_7$ γ-Naphthylpropylmethyldichlorosilane	3—4	38.5	184—185 (5)
$Cl_3SiCH_2CH_2Cl$	$Cl_3SiCH_2CH_2C_6H_5$	Al	$(Cl_3SiCH_2CH_2)_2C_6H_4$ Bis(trichlorosilylethyl)benzene	42	22.6	180—181 (8)

n_D^{20}	d_4^{20}	MR_D		Found (in %)				Empirical formula	Calculated (in %)			
		found	calc.	C	H	Si	Cl		C	H	Si	Cl
1.5549	1.2380	89.43	88.68	52.54, 52.67	4.64, 4.59	7.63, 7.27	30.48, 30.22	$C_{15}H_{15}OSiCl_3$	52.12	4.34	8.10	30.79
1.5792	1.2539	80.42	78.12	51.74, 51.65	4.64, 4.68	8.41, 8.53	33.33, 33.83	$C_{13}H_{13}SiCl_3$	51.45	4.28	9.23	35.04
1.5100	1.1109	62.70	63.04	51.45, 51.64	6.19, 6.19	10.83, 11.03	29.13, 29.06	$C_{10}H_{14}SiCl_2$	51.50	6.01	12.02	30.47
1.5238	1.2083	67.68	67.88	44.75, 44.68	4.92, 4.92	10.40, 10.52	39.17, 39.52	$C_{10}H_{13}SiCl_3$	44.86	4.86	10.47	39.81
1.5100	1.0926	67.52	67.67	53.52, 53.63	6.86, 6.84	10.55, 10.42	27.98, 27.60	$C_{11}H_{16}SiCl_2$	53.44	6.48	11.34	28.74
1.5732	1.1249	90.27	87.28	62.32, 62.44	5.85, 5.87	8.55, 8.64	20.03, 20.11	$C_{16}H_{18}SiCl_2$	62.12	5.82	9.06	22.95
1.5508	1.1620	89.20	89.15	59.00, 59.25	5.80, 5.86	8.06, 7.68	20.98, 21.13	$C_{16}H_{18}OSiCl_2$	59.08	5.53	8.61	21.85
1.5755	1.1594	80.69	78.49	59.47, 59.50	5.52, 5.52	9.72, 9.72	24.69, 24.91	$C_{14}H_{16}SiCl_2$	59.35	5 65	9.90	25.09
1·5105	1.1093	62.86	63.04	51.68, 51.74	6.11, 6.05	11.97, 12.04	27.82, 28.26	$C_{10}H_{14}SiCl_2$	51.50	6.01	62.02	30.47
1.5248	1.2109	67.68	67.88	45.08, 44.96	4.81, 4.85	10.00, 10.03	38.70, 38.44	$C_{10}H_{13}SiCl_3$	44.86	4.86	10.47	39.81
1.5115	1.0942	67.46	67.67	53.28, 53.30	6.66, 6.69	11.02, 10.90	27.79, 27.75	$C_{11}H_{16}SiCl_2$	53.44	6.48	11.34	28.74
1.5749	1.1589	80.59	78.49	59.22, 59.31	6.09, 5.97	9.49, 9.57	24.47, 24.27	$C_{14}H_{16}SiCl_2$	59.36	5.65	9.90	25.09
1.5275	1.3668	89.71	90.19	29.99, 30.13	2.81, 2.74	13.81, 13.72	51.82, 51.60	$C_{10}H_{13}SiCl_3$	29.93	2.99	13.96	53.12

TABLE 2

Original compound	Compound obtained	Yield (in %)	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D
						found
$Cl_3SiCH(C_6H_5)CH_2CH_3$	$(C_2H_5)_3SiCH(C_6H_5)CH_2CH_3$ α-Phenylpropyltriethylsilane	46	117—118° (6.5)	1.4965	0.8959	76.37
$Cl_3SiCH_2CH(C_6H_4Cl)CH_3$	$(CH_3)_3SiCH_2CH(C_6H_4Cl)CH_3$ β-Chlorophenylpropyltrimethylsilane	60.2	103—104 (6)	1.5022	0.9778	68.24
$Cl_3SiCH_2\underset{\displaystyle CH_3}{\underset{\vert}{C}}H(C_6H_5)$	$(CH_3)_3SiCH_2\underset{\displaystyle CH_3}{\underset{\vert}{C}}HC_6H_5$ β-Phenylpropyltrimethylsilane	57.1	94 (13)	1.4872	0.8723	63.33
$Cl_3SiCH_2\underset{\displaystyle CH_3}{\underset{\vert}{C}}H(C_6H_4CH_3)$	$(CH_3)_3SiCH_2\underset{\displaystyle CH_3}{\underset{\vert}{C}}H(C_6H_4CH_3)$ β-Tolylpropyltrimethylsilane	71.6	94 (6)	1.4900	0.8751	68.06
$Cl_3SiCH_2CH(C_{12}H_9)CH_3$	$(CH_3)_3SiCH_2CH(C_{12}H_9)CH_3$ β-Xenylpropyltrimethylsilane	38.8	157—158 (6)	1.5540	0.9573	89.72
$Cl_3SiCH_2CH(C_{12}H_9O)CH_3$	$(CH_3)_3SiCH_2CH(C_{12}H_9O)CH_3$ β-(Phenoxyphenyl)propyltrimethylsilane	80	164—166 (6)	1.5355	0.9829	90.03
$Cl_3SiCH_2CH(C_{10}H_7)CH_3$	$(CH_3)_3SiCH_2CH(C_{10}H_7)CH_3$ β-(Naphthyl)propyltrimethylsilane	43.4	147—148 (7)	1.5560	0.9553	81.09
$Cl_3SiCH_2CH_2CH_2C_6H_5$	$(CH_3)_3SiCH_2CH_2CH_2C_6H_5$ γ-Phenylpropyltrimethylsilane	55.9	84.5—85 (5)	1.4864	0.8701	63.40
$Cl_3SiCH_2CH_2CH_2C_6H_4Cl$	$(CH_3)_3SiCH_2CH_2CH_2C_6H_4Cl$ γ-Chlorophenylpropyltrimethylsilane	44.1	111—112 (8)	1.5021	0.9750	68.55
$Cl_3SiCH_2CH_2CH_2C_6H_4CH_3$	$(CH_3)_3SiCH_2CH_2CH_2C_6H_4CH_3$ γ-Tolylpropyltrimethylsilane	32.6	112—113 (10)	1.4885	0.8682	68.42
$Cl_3SiCH_2CH_2CH_2C_{12}H_9$	$(CH_3)_3SiCH_2CH_2CH_2C_{12}H_9$ γ-Xenylpropyltrimethylsilane	52.6	171 (6.5)	1.5529	0.9587	89.44
$Cl_3SiCH_2CH_2CH_2C_{12}H_9O$	$(CH_3)_3SiCH_2CH_2CH_2C_{12}H_9O$ γ-(Phenoxyphenyl)propyltrimethylsilane	50	163—164 (6)	1.5340	0.9817	89.92
$Cl_3SiCH_2CH_2CH_2C_{10}H_7$	$(C_2H_5)_3SiCH_2CH_2CH_2C_{10}H_7$ γ-Naphthylpropyltriethylsilane	56	188—190 (6)	1.5485	0.9585	94.08
$CH_3SiCl_2CH_2CH(C_6H_5)CH_3$	$(CH_3)_3SiCH_2CH(C_6H_5)CH_3$ β-Phenylpropyltrimethylsilane	80	79 (6.5)	1.4874	0.8717	63.39
$CH_3SiCl_2CH_2CH(C_6H_4Cl)CH_3$	$(CH_3)_3SiCH_2CH(C_6H_4Cl)CH_3$ β-Chlorophenylpropyltrimethylsilane	42	105 (7)	1.5050	0.9845	68.09
$CH_3SiCl_2CH_2CH(C_6H_4CH_3)CH_3$	$(CH_3)_3SiCH_2CH(C_6H_4CH_3)CH_3$ β-Tolylpropyltrimethylsilane	43.7	92—93 (6)	1.4898	0.8722	68.28
$CH_3SiCl_2CH_2CH(C_{12}H_9O)CH_3$	$(CH_3)_3SiCH_2CH(C_{12}H_9O)CH_3$ β-(Phenoxyphenyl)propyltrimethylsilane	65.8	164—165 (6)	1.5358	0.9868	89.72
$CH_3SiCl_2CH_2CH(C_{10}H_7)CH_3$	$(CH_3)_3SiCH_2CH(C_{10}H_7)CH_3$ β-(Naphthyl)propyltrimethylsilane	61.7	150 (6)	1.5558	0.9541	81.52
$CH_3SiCl_2CH_2CH_2CH_2C_6H_5$	$(CH_3)_3SiCH_2CH_2CH_2C_6H_5$ γ-Phenylpropyltrimethylsilane	87	78 (6.5)	1.4865	0.8664	63.68
$CH_3SiCl_2CH_2CH_2CH_2C_6H_4Cl$	$(CH_3)_3SiCH_2CH_2CH_2C_6H_4Cl$ γ-Chlorophenylpropyltrimethylsilane	72	110 (7.5)	1.5030	0.9760	68.45
$CH_3SiCl_2CH_2CH_2CH_2C_6H_4CH_3$	$(CH_3)_3SiCH_2CH_2CH_2C_6H_4CH_3$ γ-Tolylpropyltrimethylsilane	66	103—104 (7)	1.4900	0.8711	68.31
$CH_3SiCl_2CH_2CH_2CH_2C_{10}H_7$	$(CH_3)_3SiCH_2CH_2CH_2C_{10}H_7$ γ-Naphthylpropyltrimethylsilane	45	158—159 (6.5)	1.5535	0.9527	81.32

MR_D	Found (in %)				Empirical formula	Calculated (in %)			
calc.	C	H	Si	Cl		C	H	Si	Cl
76.67	77.09, 77.04	11.5, 11.33	10.94, 10.95	—	$C_{15}H_{26}Si$	76.93	11.11	11.96	—
68.62	63.49, 63.34	8.53, 8.59	11.38, 11.62	14.92, 15.32	$C_{12}H_{19}SiCl$	63.57	8.39	12.36	15.68
63.78	74.96, 74.92	10.57, 10.54	14.53, 14.27		$C_{12}H_{20}Si$	75.19	10.33	14.48	
68.35	75.90, 75.92	10.20, 10.00	12.81, 12.90		$C_{13}H_{22}Si$	75.92	10.27	13.81	
88.02	80.40, 80.40	8.93, 8.91	10.70, 10.50		$C_{18}H_{24}Si$	80.62	8.95	10.44	
89.79	76.20, 76.10	8.88, 8.71	9.35, 9.66		$C_{18}H_{24}OSi$	76.05	8.45	9.85	
79.23	79.22, 79.20	9.77, 9.89	9.95, 10.20		$C_{16}H_{22}Si$	79.34	9.09	11.57	
63.78	75.00, 75.20	10.78, 10.84	14.15, 14.42		$C_{12}H_{20}Si$	75.19	10.33	14.48	
68.62	63.46, 63.49	8.78, 8.60	12.38, 12.32	14.77, 14.96	$C_{12}H_{19}SiCl$	63.57	8.39	12.36	15.68
68.35	75.88, 75.70	10.23, 10.27	13.18, 13.58		$C_{13}H_{22}Si$	75.92	10.27	13.81	
88.02	80.82, 81.00	8.98, 8.92	9.24, 9.50		$C_{18}H_{24}Si$	80.61	8.95	10.44	
89.79	76.20, 76.20	8.44, 8.48	9.94, 9.45		$C_{18}H_{24}OSi$	76.05	8.45	9.85	
93.12	—	—	—	—	$C_{19}H_{26}Si$	—	—	—	—
63.78	—	—	—	—	$C_{12}H_{20}Si$	—	—	—	—
68.62	—	—	—	—	$C_{12}H_{19}SiCl$	—	—	—	—
68.35	—	—	—	—	$C_{13}H_{22}Si$	—	—	—	—
89.79	—	—	—	—	$C_{18}H_{24}OSi$	—	—	—	—
79.23	79.30, 79.50	9.13, 9.34	11.32, 11.00		$C_{16}H_{22}Si$	79.34	9.09	11.57	
63.78	—	—	—	—	$C_{12}H_{20}Si$	—	—	—	—
68.62	—	—	—	—	$C_{12}H_{19}SiCl$	—	—	—	—
68.35	—	—	—	—	$C_{13}H_{22}Si$	—	—	—	—
79.23	79.65, 79.70	9.38, 9.26	11.28, 11.33		$C_{16}H_{22}Si$	79.34	9.09	11.57	

224 (4b), 407 (0), 425 (1), 522 (1b), 550 (1b), 588 (2), 609 (8), 644 (4), 694 (4b), 728 (3b), 773 (0), 810 (3), 824 (3), 900 (1), 1000 (7), 1050 (3b), 1081 (3b), 1181 (5b), 1209 (4), 1243 (3), 1277 (2), 1309 (3), 1378 (4), 1407 (3b), 1451 (3b), 1611 (5 db b).

On the basis of the work of Landsberg et al. [2], it is possible to assign the frequencies at 444, 648, 806, 824, 1182, and 1378 cm^{-1} to the para-isomer, the frequencies at 520, 751, 1005, and 1242 cm^{-1} to the meta-isomer, and the frequencies at 758, 1052, and 1226 cm^{-1} to the ortho-isomer. By comparing the intensities of these lines, it was possible to conclude that the para-isomer comprised 50%, the meta-isomer 40%, and the ortho-isomer 10% of the mixture. Approximately the same ratios were also obtained for the products of the silicoalkylation of chlorobenzene.

During the silicoalkylation of benzene with α-chloropropyltrichlorosilane, there was also formed, along with the mono-substituted benzene (18%, evidently a mixture of the α- and β-isomers), disilicoalkylated benzene in a yield of 14.4%. Silicoalkylation of β-phenylethyltrichlorosilane with β-chloroethyltrichlorosilane led to bis-β-(trichlorosilyl)benzene in 32.6% yield. The majority of the substances prepared were methylated by means of CH_3MgCl.

EXPERIMENTAL

The α-, β-, and γ-chloropropyltrichlorosilanes were prepared by the method of [3].

Chlorination of methylpropyldichlorosilane. The reaction was carried out in an apparatus which has previously been described [4]. 1000 g of methylpropyldichlorosilane was taken for the reaction. The reaction was carried out by heating to a temperature of 160° in a flask. Chlorine was passed into the reaction mixture at a rate of 200 bubbles per minute (through a standard Tishchenko flask). Distillation in a column of 30 theoretical plates gave 337 g of methylpropyldichlorosilane, b.p. 124° (760 mm), n_D^{20} 1.4240, d_4^{20} 1.0423; 142.7 g (17.7%) of α-chloropropylmethyldichlorosilane, b.p. 153° (760 mm), n_D^{20} 1.4518, d_4^{20} 1.1822; 3078 (38.1%) β-chloropropylmethyldichlorosilane, b.p. 160° (760 mm), 55° (15 mm), n_D^{20} 1.4538, d_4^{20} 1.1945; 263.5 g (32.7%) of γ-chloropropylmethyldichlorosilane, n_D^{20} 1.4610, d_4^{20} 1.2267. The yields are based on the methylpropyldichlorosilane reacted.

β-Phenylpropyltrichlorosilane. The reaction of β-chloropropyltrichlorosilane with benzene was carried out in a three-necked flask fitted with a stirrer, a thermometer, a reflux condenser, and a dropping funnel. 78 g of benzene and 1.0 g of $AlCl_3$ were placed in the flask. 42.36 g (0.2 mole) of β-chloropropyltrichlorosilane was gradually introduced dropwise and with vigorous stirring. The reaction, with copious evolution of HCl, began immediately on the addition of the silane chloride. After all of the chloride had been added, the reaction mixture was heated at 80° for a period of 20 hours. 2 g of $POCl_3$ was then added, the precipitate was filtered, and the filtrate was distilled. 27 g (53.25%) of β-phenylpropyltrichlorosilane was obtained; b.p. 101-102° (6 mm). The reactions of β-chloropropyltrichlorosilane with toluene and with chlorobenzene were carried out under similar conditions; the results are presented in Table 1.

β-Xenylpropyltrichlorosilane. The reaction of β-chloropropyltrichlorosilane with diphenyl was carried out in a three-necked flask fitted with a reflux condenser, a stirrer, a dropping funnel, and a thermometer. 53.9 g of diphenyl and 0.2 g of metallic aluminum were placed in the flask. At a reaction temperature of 80°, after the diphenyl had melted, 42.36 g (0.2 mole) of β-chloropropyltrichlorosilane was gradually added with vigorous stirring. Vigorous evolution of HCl began at 90° and continued during the addition of all of the chloride. The reaction mixture was then heated for 2-3 hours at 90-100°. Distillation isolated 15 g (22.8%) of β-xenylpropyltrichlorosilane; b.p. 188-189° (6.5 mm).

All of the remaining reactions with α-, β- and γ-chloropropyltrichlorosilanes and with α-, β-, and γ-chloropropylmethyldichlorosilanes were carried out under analogous conditions. The results are presented in Table 1.

All of the substances prepared were methylated, and the results are presented in Table 2.

SUMMARY

1. The interaction of β- and γ-chloropropylsilane chlorides with aromatic compounds was studied in the presence of $AlCl_3$ or Al. It was shown that the reactivity of the γ-chloroalkylsilane chlorides in this reaction is

no lower than the reactivity of the corresponding β-isomers.

2. Silicoalkylation of benzene with γ-chloropropyltrichlorosilane gave the β- and γ-isomers in a ratio of 1:2.9. Silicoalkylation of benzene with γ-chloropropylmethyldichlorosilane gave only the γ-isomer.

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SYNTHESIS OF β-CHLOROETHYL PHENYL ACETAL

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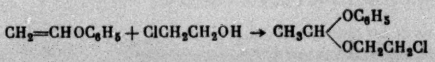
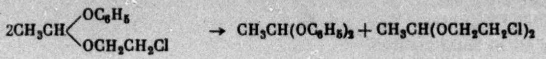
In previous work [1], the interaction of vinyl alkyl ethers with ethylene chlorohydrin was investigated, and some of the chemical properties of the resulting β-chloroethyl alkyl acetals were studied. In the present work, reactions in which ethylene chlorohydrin adds to vinyl aryl ethers were investigated using vinyl phenyl ether as an example of such ethers:



$$CH_2{=}CHOC_6H_5 + ClCH_2CH_2OH \rightarrow CH_3CH\begin{cases}OC_6H_5\\OCH_2CH_2Cl\end{cases}$$

The study of this reaction showed that, along with the reaction forming acetaldehyde β-chloroethyl phenyl acetal, disproportionation of this product to acetaldehyde diphenyl acetal and di(β-chloroethyl) acetal also proceeds according to:



$$2CH_3CH\begin{cases}OC_6H_5\\OCH_2CH_2Cl\end{cases} \rightarrow CH_3CH(OC_6H_5)_2 + CH_3CH(OCH_2CH_2Cl)_2$$

An analogous occurrence has previously been observed during a study of β-chloroethyl alkyl acetals [1].

EXPERIMENTAL

20.13 g of ethylene chlorohydrin (b.p. 129°, n_D^{20} 1.4412) was placed in a three-necked flask fitted with a reflux condenser, a mechanical stirrer, and a thermometer. 30.03 g of vinyl phenyl ether (b.p. 155°, n_D^{20} 1.5232) was gradually added, with stirring, to the flask. No signs of reaction were observed during the addition. One drop of concentrated hydrochloric acid was then added, and the mixture was heated to 145° over a period of five hours. The reaction mixture was dried over potassium carbonate and distilled under vacuum. The following fractions were collected:

First fraction, to 83° (5 mm), n_D^{20} 1.4950, 1.92 g; second fraction, 84-116° (4 mm), n_D^{20} 1.4668, 18.58 g; third fraction, 117-139° (4 mm), n_D^{20} 1.5382, 23.12 g; kettle residue, 4.0 g.

The first fraction and the kettle residue were not investigated further.

A second distillation of the second fraction isolated 11.0 g (47%) of acetaldehyde di(β-chloroethyl) acetal with a b.p. of 93-95° (6 mm), n_D^{20} 1.4548, d_4^{20} 1.1796.

Investigation of the third fraction showed that it contained 9.74 g (36%) of acetaldehyde diphenyl acetal [2] with a b.p. of 162° (10 mm), n_D^{20} 1.5587, d_4^{20} 1.0937, MR_D 63.13, calc. 62.94, and 4.07 g (8.1%) of acetaldehyde β-chloroethyl phenyl acetal (a colorless liquid, soluble in organic solvents and insoluble in water), b.p. 127-130° (8 mm), n_D^{20} 1.5108, d_4^{20} 1.1318, MR_D 53.10, calc. 52.93.

Found %: C 60.06, 59.82; H 6.76, 6.90; Cl 17.62, 17.56. $C_{10}H_{13}O_2Cl$. Calculated %: C 59.85; H 6.53; Cl 17.66.

SUMMARY

1. The interaction of vinyl phenyl ether with ethylene chlorohydrin was investigated, and acetaldehyde β-chloroethyl phenyl acetal was characterized for the first time.

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SYNTHESIS OF γ,γ'-DIPHENYLDIPROPYL ACETAL

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A method was previously proposed by one of us [1] for the preparation of acetals of the most varied structure, and some of the chemical properties of these compounds were studied. The purpose of the present work was the study of the interaction of acetaldehyde di(β-chloroethyl) acetal with a Grignard reagent. Considering that acetaldehyde di(β-chloroethyl) acetal is simultaneously a representative of both acetals and halogen compounds, it would be expected that it could react either as an alkyl halide or at the C–O bond by a Chichibabin-Elgazin reaction [2].

Summing up the investigation of this reaction, which was studied using the interaction of benzylmagnesium chloride with acetaldehyde di(β-chloroethyl)acetal, it was shown that the reaction proceeds through the chlorine atoms according to the scheme:

$$CH_3CH(OCH_2CH_2Cl)_2 + 2C_6H_5CH_2MgCl \rightarrow CH_3CH(OCH_2CH_2CH_2C_6H_5)_2,$$

while in our previous investigations [3], it was found that the interaction of a Grignard reagent with symmetrical and with mixed acetals not containing halogen in the alcohol radicals proceeds at the C–O bonds.

EXPERIMENTAL

To the Grignard reagent, prepared from 8 g of magnesium and 42 g of benzyl chloride, was gradually added 23 g of acetaldehyde di(β-chloroethyl) acetal [4]. When the resulting viscous reaction mixture was further heated, it unexpectedly foamed and then solidified. After the mass was cooled, it was treated with 5% acetic acid until it had completely dissolved. The ether layer was separated, washed with water, dried over sodium sulfate, and placed in a distillation flask. The ether was distilled, and the residue (19.8 g) was distilled under vacuum. The following fractions were obtained: 1st fraction, 75-120° (11 mm), 2.05 g; 2nd fraction, 121-181° (11 mm), 5.67 g; 3rd fraction, 182-260° (10 mm), 2.9 g; kettle product, 2.9 g (dibenzyl). The first and third fractions were not investigated. During the investigation of the 2nd fraction, 3.09 g (8.4%) of acetaldehyde di(γ-phenylpropyl) acetal was isolated. It was a colorless liquid with an aromatic odor, readily soluble in organic solvents and insoluble in water.

B.p. 111° (6 mm), n_D^{20} 1.5288, d_4^{20} 1.0073, MR_D 90.64; calc. 91.24.

Found %: C 80.26, 80.52; H 8.60, 8.75. $C_{20}H_{26}O_2$. Calculated %: C 80.53; H 8.72.

SUMMARY

The interaction of acetaldehyde di(β-chloroethyl) acetal with benzylmagnesium chloride was investigated. It was established that the reaction proceeds through the chlorine atoms, and not at the C–O bonds. Acetaldehyde di(γ-phenylpropyl) acetal was described for the first time.

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INVESTIGATIONS IN THE FIELD OF THE SYNTHESIS AND CONVERSIONS OF OXYGEN-CONTAINING ORGANOSILICON COMPOUNDS

ON THE INTERACTION OF VINYLALKYLCHLOROSILANES WITH VINYL BUTYL ETHER AND VINYL LACTAMS

M.F. Shostakovskii, D.A. Kochkin, V.A. Neterman and F.P. Sidel'kovskaia

It is known from the literature that vinylalkylchlorosilanes do not polymerize even when heated in the presence of either peroxides [1] or ionic [2] catalysts, or else they form polymers of comparatively low molecular weight. It appeared to be of interest to investigate whether polymerization or copolymerization of these compounds with other unsaturated compounds is possible. We established that vinylalkyldihalosilanes, for example, vinylethyldichloro- and vinyltrichlorosilane, do not polymerize on long heating (100°, 200 hours) in the presence of either ionic ($SnCl_2$, $SnCl_4$, BF_3) or free radical (triethylaluminum, azobisisobutyronitrile) initiators. At the same time, unsaturated organosilicon compounds containing a double bond in the middle of the silicon-carbon chain or containing two conjugated double bonds have a tendency toward polymerization, either under the influence of radical initiators or through the action of light. Thus, for example, tetrachlorodiethylsilylbutene [3], $C_2H_5SiCl_2CH_2CH_2CH=CHSiCl_2C_2H_5$ has been polymerized to a solid, alcohol- and ether-insoluble polymer by heating at 100° for 80 hours in the presence of azobisisobutyronitrile. The action of light over a period of five months converted ethyldichlorobutadienylsilane to a transparent, rubbery mass.

The following pairs of monomers were investigated in the study of the copolymerization of vinylalkylchlorosilanes: vinylmethyl- and vinylethyldichlorosilanes with vinyl butyl ether, vinylcaprolactam, and vinylpyrrolidone. The experiments were carried out at room temperature and at 60° and both with and without azobisisobutyronitrile present. It was found that under these conditions, vinylalkylchlorosilanes neither polymerize nor copolymerize. They are initiators of the polymerization of vinyl butyl ether, vinylcaprolactam, and vinylpyrrolidone.

However, in the case of the interaction of vinylalkyldichlorosilanes with vinylpyrrolidone, in addition to vinylpyrrolidone polymer, there was obtained a small amount of products containing silicon and nitrogen in the molecule; these were apparently produced by the interaction of these monomers. The initiation of polymerization by vinylalkylhalosilanes was probably due to the liberation of hydrogen chloride, which causes ionic polymerization of unsaturated compounds. For comparison, experiments were carried out on the polymerization of vinyl butyl ether, vinylcaprolactam, and vinylpyrrolidone in the presence of a saturated alkylhalosilane, namely, ethyltrichlorosilane, which also readily liberates hydrogen chloride. In this case also, polymerization of the indicated unsaturated compounds was observed, which indicates that the alkylhalosilane and the vinylalkylhalosilanes behave analogously. Thus, vinylalkyl- and alkylhalosilanes can be used as polymerization initiators.

EXPERIMENTAL

The vinylmethyl- and vinylethyldichlorosilanes were prepared by the previously described [3] vinylation of methyl- and ethyldichlorosilanes. The vinylcaprolactam and vinylpyrrolidone were synthesized by vinylation of caprolactam and pyrrolidone.

All polymerization experiments were carried out in sealed tubes into which were introduced the calculated amounts of the monomers (total amount was 5 g; 0.2% initiator); the tubes were sealed, and then were heated at

60° for 72 hours in some cases, and were allowed to stand at room temperature for several days in other cases. The polymeric products obtained from vinyl butyl ether and vinylalkyldichlorosilane were freed from unreacted monomers by treatment with ethyl alcohol, and were then vacuum dried to constant weight. Molecular weights of the polymers were determined cryoscopically. Molecular weights of 5770 and 5200 were found for the products from Experiments 1 and 2, respectively.

The polymers formed during the reactions of vinylpyrrolidone and vinylcaprolactam with the vinylalkyldichlorosilanes were precipitated from benzene solution with ether, dried under vacuum to constant weight, and analyzed for content of C, H, Si, N, and Cl. During the reaction of vinylpyrrolidone and of vinylcaprolactam with vinylethyldichlorosilane at 60°, tarry, heterogeneous, dark masses were formed, the separation of which was difficult.

The products from the reaction of vinylpyrrolidone and vinylmethyldichlorosilane, both with and without azobisisobutyronitrile present, contained silicon. In order to fractionate these polymers, they were treated with ethyl alcohol. This treatment gave small amounts of alcohol-insoluble powders (0.3%), which were apparently products of the interaction of vinylmethyldichlorosilane and vinylpyrrolidone.

Composition of the powder obtained from the experiment using an initiator, %: C 30.00, 29.91; H 5.98, 5.94; Cl 0.26, 0.30; Si 33.20, 33.53; N 1.68, 1.78. Composition of the powder from the experiment without an initiator, %: C 27.47, 27.04; H 5.78, 5.59; Cl – none; Si 32.90, 33.63; N 4.29, 4.02.

SUMMARY

1. The interaction of vinylalkyl- and alkylhalosilanes with vinyl butyl ether, vinylcaprolactam, and vinylpyrrolidone was investigated.

2. The monomer pairs studied formed practically no copolymers.

3. The major products of the interaction of the indicated compounds were polymers of vinyl butyl ether, vinylcaprolactam, and vinylpyrrolidone.

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SYNTHESIS OF ALKENYL-α-CN-ISOPROPOXYSILANES

V.M. Vdovin and A.D. Petrov

Alkyl- and aryl-α-CN-isopropoxysilanes have been investigated in a number of researches [1-3]. The interest in these compounds is explained, on the one hand, by the ease of introduction of a CN-containing radical into the molecule of an organosilicon compound, and, on the other hand, by the tendency of the Si–O bond, which is screened by a branch radical, toward hydrolysis [2, 3]. In a previous paper [2], we reported on the synthesis of a polymeric CN-containing product by hydrolysis of $C_2H_5SiCl_2[OC(CH_3)_2CN]$. The aim of the present investigation was the synthesis of α-CN-isopropoxysilanes containing unsaturated radicals, which are also needed for the production of CN-containing organosilicon polymers. Both alkenyl-α-CN-isopropoxysilanes [4] and alkenyl-α-CN-isopropoxysilanes containing hydrogen attached to the silicon [5, 6] were of interest. The original alkenylchlorosilanes, both with and without an Si–H bond, were prepared by direct synthesis [7, 8] and also by photochemical chlorination and dehydrochlorination of ethyltrichlorosilane [9].

These chlorosilanes were converted to the corresponding α-CN-isopropoxylsilyl derivatives by interaction with acetone cyanohydrin:

$$R_mSiCl_n + n\cdot HOC(CH_3)_2CN \xrightarrow{nC_5H_5N} R_mSi[OC(CH_3)_2CN]_n + nC_5H_5N\cdot HCl,$$

$$\text{where } m=1 \text{ or } 2,\ m+n=4, \text{ a } R= CH_2{=}CH{-}CH_2,\ CH_2{=}\underset{CH_3}{\underset{|}{C}}{-}CH_2 \text{ and } CH_2{=}CH.$$

However, the interaction of allyl- and methallyldichlorosilanes with acetone cyanohydrin and pyridine, with the latter two in excess over the calculated amounts, unexpectedly gave alkenyltri-α-CN-isopropoxysilanes, in addition to the expected alkenyl-di-α-CN-isopropoxysilanes containing an Si–H group. In a control experiment, the interaction of $CH_2=\underset{CH_3}{\underset{|}{C}}-CH_2-SiH[OC(CH_3)_2CN]_2$ with acetone cyanohydrin and pyridine* also gave $CH_2=\underset{CH_3}{\underset{|}{C}}-CH_2-Si[OC(CH_3)_2CN]_3$. Similarly, from CH_3SiCl_2H was obtained $CH_3Si[OC(CH_3)_2CN]_3$ according to the equation:

$$CH_3SiCl_2H + 4HOC(CH_3)_2CN \xrightarrow{4C_5H_5N} CH_3Si[OC(CH_3)_2CN]_3 + 2C_5H_5N\cdot HCl + \\ + H_2 + 2C_5H_5N + HOC(CH_3)_2CN.$$

It is curious that other tertiary alcohols react with Si–H-containing silanes only under rigorous conditions – heating in an autoclave in the presence of alkali [10]. The ease with which acetone cyanohydrin reacts both with Si–H and with Si–Cl [1-3] may obviously be explained by the activating effect of the polar CN group on the hydroxyl of the alcohol.

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*The use of pyridine as a catalyst for reactions between Si–H-containing silanes and acetone cyanohydrin is the most interesting, because mineral bases are not applicable in the case of acetone cyanohydrin, since they cleave cyanohydrins with the formation of ketones and hydrochloric acid.

We also studied the feasibility of introducing an allyloxy radical into the molecule of alkyl-α-CN-isopropoxychlorosilanes by the reaction:

$$(CH_3)_2Si[OC(CH_3)_2CN]Cl + HOCH_2{-}CH{=}CH_2 \xrightarrow{C_5H_5N}$$
$$\rightarrow (CH_3)_2Si(OCH_2{-}CH{=}CH_2)[OC(CH_3)_2CN] + C_5H_5N \cdot HCl,$$

and in this case, along with the product expected from the above equation, $(CH_3)_2Si(OCH_2-CH=CH_2)_2$ and $(CH_3)_2Si[OC(CH_3)_2CN]_2$ were also obtained. The formation of these latter two compounds is explained by transesterification:

$$(CH_3)_2Si(OCH_2{-}CH{=}CH_2)[OC(CH_3)_2CN] \rightleftarrows (CH_3)_2Si(OCH_2CH{=}CH_2)_2 +$$
$$+ (CH_3)_2Si[OC(CH_3)_2CN]_2$$

or by disproportionation of the allyloxy and α-cyanoisopropoxy groups.

EXPERIMENTAL

The properties of the compounds prepared are presented in the Table. Compounds (III)-(VI) were prepared by the method of [1] from equivalent amounts of the reagents; (VII) was also prepared by the method of [1] with a ratio of $CH_2=CHSiCl_3$ to acetone cyanohydrin of 3 : 1.

Interaction of methallyldichlorosilane with acetone cyanohydrin. 37 g (0.435 mole) of acetone cyanohydrin was added, over a period of 0.5 hour and with stirring, to 27 g (0.174 mole) of methallyldichlorosilane and 34.4 g (0.435 mole) of pyridine; the temperature of the reaction mixture rose slightly due to exothermic heat, but no precipitate of pyridine salt formed. The contents of the flask were then heated for three hours to incipient boiling of the benzene, and was allowed to stand overnight. The benzene solution was filtered from the precipitate, the benzene was distilled, and the viscous oil, which evolved a gas on standing, was distilled under vacuum. A rough distillation gave the following fractions: 1st fraction, 138-142° (9 mm), 18.2 g; 2nd fraction, 170-172° (9 mm), 3.6 g. (II) was obtained by a second distillation of the first fraction. The material which constituted the second fraction had the following properties: n_D^{20} 1.4390 and d_4^{20} 1.0082, and it was identical with (VI).

The interaction of allyldichlorosilane (0.382 mole) with acetone cyanohydrin (0.9 mole) in the presence of pyridine (0.9 mole) in 400 ml of benzene gave (I) and also a substance with a b.p. of 178-179° (9 mm), n_D^{20} 1.4340, d_4^{20} 1.0132, which was similar to (V); the yield of the latter compound was 27% calculated on the allyldichlorosilane.

When the reactants $CH_2=CHCH_2SiCl_2H$, $HOC(CH_3)_2CN$, and C_5H_5N, in amounts of 0.25, 0.5 and 0.5 mole, respectively, and 350 ml of benzene were reacted, (I) was obtained in 67% yield, but no appreciable amounts of (V) were detected.

The interaction of 12.5 g (0.05 mole) of methallyl-di-α-CN-isopropoxysilane with 8.3 g (0.1 mole) of acetone cyanohydrin and 8 g (0.1 mole) of pyridine, by an analogous method but with an eight-hour heating of the reaction mixture to the boiling point of benzene, gave substance (VI) with a b.p. of 160-162° (5 mm), n_D^{20} 1.4394, d_4^{20} 1.0083. The yield was 61.5%.

Methyltri-α-CN-isopropoxysilane was prepared from 23 g (0.2 mole) of methyldichlorosilane, 68 g of acetone cyanohydrin, and 63 g of pyridine in 200 ml of benzene. After the reaction mixture had been heated for 16 hours, the usual treatment gave 27.2 g of a substance with a b.p. of 166-168° (10 mm), n_D^{20} 1.4229, d_4^{20} 1.0177. Literature data [2] for this substance: b.p. 126° (1 mm), n_D^{20} 1.4219, d_4^{20} 1.0155.

Found %: N 14.43, 14.34. $C_{13}H_{21}O_3N_3Si$. Calculated %: N 14.27.

Interaction of dimethyl-α-CN-isopropoxychlorosilane with allyl alcohol. 7.2 g (0.124 mole) of allyl alcohol was added, over a period of 0.5 hour, to a solution of 22 g (0.124 mole) of dimethyl-α-CN-isopropoxychlorosilane and 9.8 g (0.124 mole) of pyridine in 150 ml of benzene. A precipitate appeared after the first drop of allyl alcohol, and the reaction became exothermic. The contents of the flask were stirred for another one hour, and the reaction mixture was then treated by the usual method. The following fractions were obtained by vacuum distillation: 1st fraction, 80-95° (40 mm), 5 g, with a sharp odor; 2nd fraction, 102-108° (40 mm), 10.2 g, also with a sharp odor; 3rd fraction, 92-101° (5 mm), 5.1 g, viscous, odorless oil. Fractionation of the first

Sub-stance No.	Name and structural formula of substance	Yield (%)	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D		Empirical formula	N (в %)	
						calc.	found		calc.	found
(I)	Allyldi-α-CN-isopropoxysilane $CH_2{=}CHCH_2SiH[OC(CH_3)_2CN]_2$	33	116—117 (6)	1.4330	0.9697	63.74	63.74	$C_{11}H_{18}O_2N_2Si$	11.75	11.66, 11.97
(II)	Methallyldi-α-CN-isopropoxysilane $CH_2{=}C(CH_3)CH_2SiH[OC(CH_3)_2CN]_2$	41.5	138—139 (9)	1.4352	0.9653	68.24	68.23	$C_{12}H_{20}O_2N_2Si$	11.09	11.01, 10.95
(III)	Diallyldi-α-CN-isopropoxysilane $(CH_2{=}CHCH_2)_2Si[OC(CH_3)_2CN]_2$	60.6	139—140 (5)	1.4479	0.9672	77.08	77.04	$C_{11}H_{22}O_2N_2Si$	10.42	10.58
(IV)	Vinyltri-α-CN-isopropoxysilane $CH_2{=}CHSi[OC(CH_3)_2CN]_3$	48	138 (3)	Cryst. matl., m.p. 36.5°, from ether				$C_{14}H_{21}O_3N_3Si$	13.84	13.43, 13.20
(V)	Allyltri-α-CN-isopropoxysilane $CH_2{=}CHCH_2Si[OC(CH_3)_2CN]_3$	46	169 (6)	1.4337	1.0127	82.54	82.60	$C_{15}H_{23}O_3N_3Si$	13.40	13.04, 13.21
(VI)	Methallyltri-α-CN-isopropoxysilane $CH_2{=}C(CH_3)CH_2Si[OC(CH_3)_2CN]_3$	63	158 (4)	1.4392	1.0078	87.04	87.53	$C_{16}H_{25}O_3N_3Si$	12.52	12.51, 12.35
(VII)	Vinyl-α-CN-isopropoxydichlorosilane $CH_2{=}CHSiCl_2[OC(CH_3)_2CN]$	84	84 (10.5)	1.4390	1.1479	48.13	48.14	$C_6H_9ONCl_2Si$ *	—	—
(VIII)	Dimethylallyloxy-α-CN-isopropoxysilane $(CH_3)_2Si[OCH_2CH{=}CH_2][OC(CH_3)_2CN]$		105—106 (40)	1.4178	0.9289	54.26	53.91	$C_9H_{17}O_2NSi$	7.02	6.91, 6.88
(IX)	Ethyldiallyloxy-α-CN-isopropoxysilane $C_2H_5Si[OCH_2CH{=}CH_2]_2[OC(CH_3)_2CN]$		106—108 (4)	1.4294	0.9674	68.44	68.08	$C_{12}H_{21}O_3NSi$	5.52	5.42, 5.25

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* Analysis for nitrogen was not carried out. Found % Si 13.28, 13.24. Calculated % Si 13.32.

fraction gave a substance with a b.p. of 86-87° (42 mm), n_D^{20} 1.4172, d_4^{20} 0.8830. Literature data [6] for $(CH_3)_2Si(OCH_2CH=CH_2)_2$: b.p. 155.8° (745 mm), n_D^{20} 1.4170, d_4^{20} 0.8822.

Fractionation of the second fraction gave substance (VI). A second distillation of the third fraction gave $(CH_3)_2Si[OC(CH_3)_2CN]_2$ with a b.p. of 125-127° (21 mm), n_D^{20} 1.4166, d_4^{20} 0.9640. Literature data [3]: b.p. 124-126° (21 mm), n_D^{20} 1.4174, d_4^{20} 0.9644.

(IX) was similarly obtained from equivalent amounts of ethyl-α-CN-isopropoxydichlorosilane, allyl alcohol, and pyridine. The substance (IX) was also separated, with difficulty, from the complex mixture of ethers by fractional distillation.

SUMMARY

1. Seven alkenyl-α-CN-isopropoxysilanes and two allyloxy-α-CN-isopropoxysilanes, none of which have been described in the literature, were synthesized.

2. The feasibility of obtaining alkenyl- and alkyl-α-CN-isopropoxysilanes by the interaction of acetone cyanohydrin with Si−H-containing silanes in the presence of pyridine was demonstrated.

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ORGANOMAGNESIUM SYNTHESIS WITH CARBON SUBOXIDE. I

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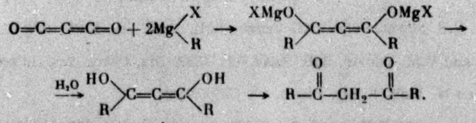
Since carbon suboxide is an unusual ketone and behaves in a manner similar to ketene in many reactions, it might be expected that organomagnesium synthesis by means of carbon suboxide would lead to the production of symmetrical β-diketones according to the scheme:



Our assumption was vindicated; diacetylmethane [2,4-pentanedione], dipropionylmethane [3,5-heptanedione], divalerylmethane [5,7-undecanedione], dibenzoylmethane [1,3-diphenyl-1,3-propanedione], and di(phenylaceto)methane [1,5-diphenyl-2,4-pentanedione] were prepared by means of carbon suboxide. The yields of β-diketones varied within rather wide limits (from 15 to 70%).

EXPERIMENTAL

The ether solutions of carbon suboxide were prepared by the method of Staudinger [1].

Preparation of diacetylmethane. To an ether solution of methylmagnesium iodide, prepared from 8.0 g of methyl iodide, was added 240 ml of an ether solution of carbon suboxide (2.05 g of C_3O_2). The reaction mixture was stirred for half an hour. The organomagnesium complex was then decomposed with hydrochloric acid, the ether layer was separated, and the aqueous layer was extracted with ether. After distillation of the ether, the residue was distilled at 132-135° (according to the literature [2], diacetylmethane has a b.p. of 135-136°). 0.39 g (15%) of the substance (n_D^{20} 1.4539, d_4^{20} 0.9701) was obtained. A qualitative reaction with ferric chloride for the presence of an enol group was positive. The amide of 3,5-dimethylpyrazole-1-carboxylic acid, m.p. 111-112°, was prepared from the diacetylmethane; the m.p. is in agreement with the literature value [2].

Dipropionylmethane was prepared by the above method from 5.5 g of ethyl bromide and 180 ml of an ether solution of carbon suboxide (1.50 g of C_3O_2). 1.4 g (50%) of a fraction boiling at 72-74° (25 mm), n_D^{20} 1.4050, d_4^{20} 0.9444, was obtained. According to the literature [3], dipropionylmethane has a b.p. of 80° (30 mm). The test for the enol group was positive.

Divalerylmethane was prepared from 8.0 g of butyl chloride and 130 ml of an ether solution of carbon suboxide (1.0 g of C_3O_2). 1.2 g (51%) of the material was obtained; n_D^{20} 1.4567, d_4^{20} 0.9258, b.p. 84-86° (17 mm), which is in approximate agreement with the literature value [4]. The test for the enol group was positive.

Dibenzoylmethane was prepared from 15 g of bromobenzene and 60 ml of an ether solution of carbon suboxide (0.5 g C_3O_2). After distillation of the ether and treatment of the oily residue with 20% NaOH, crystals were obtained with an m.p. of 71-73°, which is in agreement with the literature value [5]. The qualitative test for the presence of the enol group was positive. The yield was 0.93 g (65%).

Di(phenylaceto)methane was prepared from 13 g of benzyl chloride and 60 ml of an ether solution of carbon suboxide (0.48 g of C_3O_2). The resulting oily residue soon crystallized. M.p. 51-52° (from 70% ethyl alcohol). The test for the enol group was positive. The yield was 1.03 g (68%).

Found %: C 12.40; H 6.06. M (Rast) 250. $C_{17}H_{16}O_2$. Calculated %: C 12.70; H 6.35. M 252.

The complete analogy with the preceding reactions and the analytical data confirm that the synthesized substance was di(phenylaceto)methane.

SUMMARY

1. It was shown that the interaction, in the cold and in an ethereal medium, of carbon suboxide with organomagnesium halides results in the formation of symmetrical aliphatic and aromatic β-diketones.

2. In individual cases, the interaction of carbon suboxide with organomagnesium halides can apparently serve as a method for the preparation of symmetrical β-diketones.

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THE EFFECT OF LOW MOLECULAR WEIGHT MATERIALS ON THE PHOTOCHEMICAL DEGRADATION OF POLYETHYLENE TEREPHTHALATE

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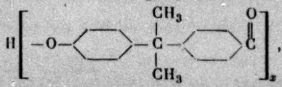
Up to the present time, the literature has presented only a small amount of information on the photochemical degradation of polyesters in general and of polyethylene terephthalate in particular. Griehl [1] reported on the changes in the tensile strength of certain fibers occurring under the influence of ultraviolet irradiation. In comparison with Perlon and viscose silk, polyethylene terephthalate displayed the least drop in tensile strength. According to the data of Coleman [2], the intrinsic viscosity of a polyethylene terephthalate sample changed by only 1-1.5% after a 300-hour irradiation with ultraviolet light. Under the same conditions, the intrinsic viscosity of a copolymer of polyethylene terephthalate and polyethylene glycol changed by 40%. The results of an investigation of the stability to light of 1C-312 and 1C-312-2 polyesters have been published [3]. The compositions of these polyesters were not reported. The absorption of these polyesters in the ultraviolet region lay in the region of 3500 A. The absorption in this region of the spectrum increased with an increase in the duration of the irradiation. A number of compounds were investigated with the aim of finding the best stabilizers. The most effective stabilizers were derivatives of o-hydroxybenzophenone. Salol exhibited the best protective effect. There have also been reports that organic compounds having a functionality greater than two are stabilizers for linear polyesters. Such compounds must contain ester groups [4]. Schnell [5] presented data on the effects of the irradiation of polycarbonate films,  , prepared from 2,2-(4,4'-dihydroxydiphenyl)propane and phosgene. The mechanical properties of the film samples had not changed after 72 hours of irradiation with a Hanau-300 lamp placed at a distance of 29 cm from the sample and at an angle of 45°. These data represent the extent of the information available in the literature on the photochemical degradation of polyesters.

In the present investigation, we studied the changes in the properties of polyethylene terephthalate (Lavsan) caused by the action of the total radiation from a PRK-2 lamp and also by the action of a narrower portion of the spectrum, the portion lying in the range 300-320 mμ (the mercury line is at 313 mμ). At the same time, an attempt was made to follow the effect of certain low molecular weight compounds on the course of the changes in the properties of polyethylene terephthalate under the influence of ultraviolet irradiation.

The absorption spectra of the samples of polyethylene terephthalate film at our disposal were not uniform, but varied somewhat from sample to sample. Sometimes, a uniform absorption down to 310 mμ was observed; at other times, weak maxima in the absorption spectra were noted at 345 and 428 mμ. These data differ somewhat from the published data [6], and this can apparently be explained by certain differences in the composition of the polyesters.

In order to clarify the effect of low molecular weight organic compounds on the course of the photochemical degradation of polyethylene terephthalate, substances with different structures were used [7]. Each of these compounds absorbed in the region of 250-320 mμ, and the absorption extended further into the region of longer wavelengths. The additives used in the present investigation were salol, the diethyl ester of dihydroxyterephthalic acid, β-methylumbelliferone, and 2-o-hydroxyphenylbenzoxazole. The absorption spectra of these compounds were presented in a previous communication [7].

The organic compounds were introduced into the finished polyethylene terephthalate films. For this purpose, the samples of film were swollen in solutions containing the required substances. The amount of material introduced into the film was not determined accurately. The penetration of the organic compound into the polymer film could be estimated only qualitatively by the change in the color of the luminescence of the film sample after swelling corresponded to the color of the luminescence of the substance serving as the additive. The prepared film samples were tested under the same conditions as the samples of polyester containing no additive.

As was indicated above, irradiation of the samples was by a PRK-2 quartz mercury lamp. The effect of wavelengths in the 300-320 mμ region was investigated separately. This region was of interest to us, because the 300-320 mμ region of the solar spectrum has a high intensity, and the behavior of the polyethylene terephthalate films toward the action of waves of this length permitted estimation, to a certain extent, of the stability of the polymer toward exposure to sunlight.

Changes in the molecular weight, the mechanical properties, and the spectral characteristics were determined after irradiation of the film samples with ultraviolet light.

EXPERIMENTAL

Samples of the polyethylene terephthalate film, with a thickness of 30-40 μ and oriented in the longitudinal direction, were submerged in a 1% solution of the organic compound in a mixture of Chlorex and ethyl alcohol (2 : 3). The swelling time of the films in the solution was 18 hours. After the expiration of this period, the samples were taken from the solution, washed well with alcohol, dried in air, and stored in the dark. Some of the experiments were repeated with samples of polyethylene terephthalate film, the thickness of which was also 30-40 μ. These samples were submerged in the solution of the additive for only three hours. In specific cases, the organic compound used as the additive was dissolved in a mixture of Chlorex and ethyl alcohol taken in a ratio of 1 : 3. In these experiments, diethyl 2,5-dihydroxyterephthalate and 2-o-hydroxyphenylbenzoxazole served as the additives.

Irradiation of the film samples was carried out at 20° with light from a PRK-2 lamp placed at a distance of 50 mm from the sample. The length of the irradiation was 10 hours. In order to maintain this regime, the entire apparatus was placed in a glass, thermostatted bath filled with distilled water. The 300-320 mμ region was separated from the total spectrum of the quartz-mercury lamp by means of a liquid filter which was poured into the bath together with the distilled water [7]. The irradiation time of the samples was 100 hours in the first experiments and 50 hours in the repeat experiments.

Samples of the film before and after irradiation were tested in a Poliani-type dynamometer [as in Russian] to determine tensile strength and elongation. Elongation of the film was across the orientation of the polymer.

The molecular weight of the polyethylene terephthalate was determined by the viscosimetric method. For this purpose, the viscosity of an 0.5% solution of the polymer (film) in m-xylene was determined at 25°. The equation proposed by Turska-Kusmiery and Skwarski [8] was used to calculate the molecular weight:

$$[\eta] = 5.517 \cdot 10^{-4} \cdot M^{0.700},$$

$[\eta] = \eta_{sp}/c/(1 + 0.66\eta_{sp})$, where c is the concentration, 0.5%.

The change in the absorption spectra was determined for the samples of the film before and after irradiation.

The absorption spectra of the samples were taken with a spectrophotometer with a high-speed recording attachment.

DISCUSSION OF RESULTS

Ten-hour irradiation of polyethylene terephthalate film with light from a PRK-2 quartz-mercury lamp under the conditions of our experiments undoubtedly leads to degradation of the polymer. This is indicated primarily by the mechanical properties of the film and, chiefly, by the elongation at break. As seen from Figs. 1 and 2, the elongation at break of two samples of polyethylene terephthalate film of different thickness decreased by a factor of 6-8 after a ten-hour exposure as compared to the original value. The tensile strength of the samples also decreased after exposure, but less significantly than the elongation. As a practical matter, the samples became less elastic, brittle, and unsuitable for use. The molecular weight of the exposed samples decreased from 14,300 to 12,000.

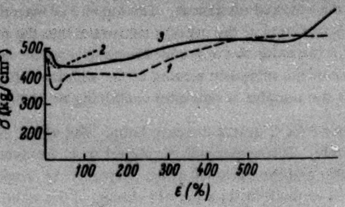


Fig. 1. Elongation curves for a sample of polyethylene terephthalate (0.003 cm): 1) before irradiation; 2) after 10-hour exposure to a PRK-2 lamp; 3) after 50-hour exposure to 300-320 mμ radiation.

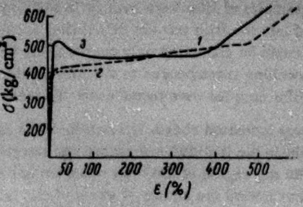


Fig. 2. Elongation curves of a sample of polyethylene terephthalate (0.01 cm): 1) before exposure; 2) after 10-hour exposure to a PRK-2 lamp; 3) after 50-hour exposure to 300-320 mμ radiation.

In addition, it must be pointed out that during the course of the photochemical degradation of polyethylene terephthalate, we did not observe the formation of insoluble material. It is quite probable that the polymer molecule, under the influence of photons, breaks down into small fragments, and the formation of an insoluble three-dimensional product, if it proceeds at all, does so to a very slight extent.

The intensity of the absorption in the ultraviolet region of the spectrum increased slightly with an increase in exposure, and the appearance of maxima was noted in the region of 330-344 mμ (Fig. 3). These results are in agreement with data presented in the literature for other polyesters [3]. The increase in the intensity of the absorption in the ultraviolet region of the spectrum after exposure of the polymer can apparently be explained by the appearance of more unsaturation caused by the decomposition of the molecule as a result of photochemical degradation. Moreover, the absorption was shifted further into the visible part of the spectrum, which also confirms the appearance in the polymer molecule of new bonds, possibly aromatic in character. The effect of exposure to radiation in the 300-320 mμ region is very slight, and is indicated chiefly by somewhat of a decrease in the tensile strength of the samples.

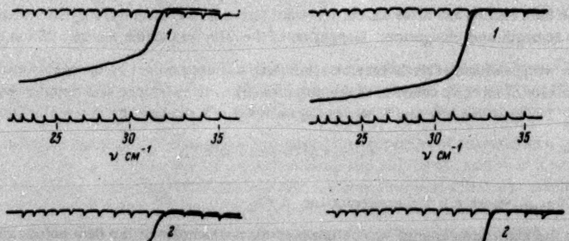


Fig. 3. Absorption spectra of two samples of polyethylene terephthalate films: 1) before exposure; 2) after 10-hour exposure to a PRK-2 lamp.

Before proceeding to a discussion of the results obtained with samples of polyethylene terephthalate with added organic compounds, we should pause for a moment to consider the effect of the solvents used for swelling the films on the properties of these films before exposure. As already noted, a mixture of Chlorex and alcohol

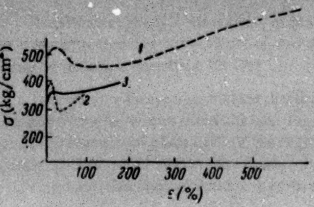


Fig. 4. Elongation curves for polyethylene terephthalate samples (0.01 cm) treated with solvent: 1) before exposure; 2) after 10-hour exposure to a PRK-2 lamp; 3) after 50-hour exposure to 300-320 mμ radiation.

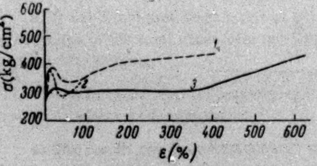


Fig. 5. Elongation curves for the sample of polyethylene terephthalate with 2-o-hydroxyphenylbenzoxazole additive: 1) before exposure; 2) after 10-hour exposure to a PRK-2 lamp; 3) after 50-hour exposure to 300-320 mμ radiation.

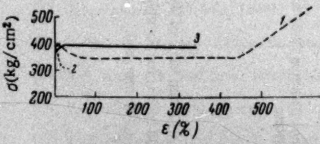


Fig. 6. Elongation curves of a polyethylene terephthalate sample (0.01 cm) with diethyl dihydroxyterephthalate additive: 1) before exposure; 2) after 10-hour exposure to a PRK-2 lamp; 3) after 50-hour exposure to 300-320 mμ radiation.

in two different ratios, namely, 2 : 3 and 1 : 3, were used during the course of the investigation. The soaking time of the films was also varied from 18 hours in the first case to three hours in the second case. We established that the solvent undoubtedly has an effect on the properties of polyethylene terephthalate, even before exposure of the polymer to ultraviolet irradiation. The mechanical properties of the samples of polyethylene terephthalate film were appreciably worse after swelling, the mixture containing Chlorex and alcohol in a 2 : 3 ratio having the greater effect.

In Fig. 4 are presented the results of the irradiation of samples of polyethylene terephthalate film treated with a mixture of Chlorex and alcohol (1 : 3). The additives introduced into the film samples decreased the tensile strength of the films in comparison with the samples treated with solvent alone. In addition, the elasticity of the films containing additives was slightly lower than that of the solvent-treated samples; this indicates some incompatibility of the polyester and the substance used (see Table). As would be expected, the effect of the addition of organic compounds was developed only in samples exposed to light in the region of 300-320 mμ.

β-Methylumbelliferone displayed no stabilizing effect against the process of photochemical degradation of the polyethylene terephthalate. This appeared as a deterioration of the mechanical properties of the exposed samples containing this additive (see Table). The absorption spectrum of this same sample after exposure showed a small increase in absorption in the ultraviolet region. The results of a previous investigation [7] showed that β-methylumbelliferone decomposes under the conditions of the experiment. We assume that, since the experimental conditions were unchanged in the present case, the β-methylumbelliferone undoubtedly behaved the same, and, decomposing under the action of photons, formed free radicals which accelerated the degradation of the polyester.

The addition of salol caused some improvement of the mechanical properties of the film after exposure. The break strength and deformation were increased in comparison with the unexposed film sample. As has already been indicated, the protective properties of salol with respect to polyesters has been reported in the literature [3]. However, salol has an unfavorable effect on the mechanical properties of polyethylene terephthalate before exposure, appreciably decreasing the tensile strength of the sample. Absorption in the ultraviolet region of the spectrum did not increase after exposure of the sample containing salol. The positive effect displayed by salol on exposure of the polyethylene terephthalate to 300-320 mμ radiation can be explained on the basis that, being an inhibitor, it can slow down the development of free radicals during the course of their formation under the action of radiation. Dwelling for a moment on the positive effect displayed by salol, it seems to us desirable to recall the results presented in a previous communication [7]. In this investigation, a positive, but only insignificant effect of salol on the course of the photochemical degradation of polystyrene was detected.

Results of Mechanical Tests on Samples of Polyethylene Terephthalate Before and After Exposure*

Sample No.	Film sample tested	Film thickness (in cm)	Before exposure		After exposure to u.v. from PRK-2 lamp (10 hrs)		After exposure to 300-320 $m\mu$ radiation**	
			ε (%)	σ (kg/cm^2)	ε (%)	σ (kg/cm^2)	ε (%)	σ (kg/cm^2)
1	Film without additive	0.01	560	606	104	403	385	513
2	Film without additive	0.003	660	628	79	448	609	635
3	Film No. 1 treated with a mixture of Chlorex and alcohol (1:3) for 3 hours	0.01	686	534	43	329	207	400
4	Film No. 1 treated with the same Chlorex-alcohol mixture for 3 hours. Additive – diethyl dihydroxyterephthalate	0.01	505	460	90	350	348	384
5	Film No. 1 treated with the same Chlorex-alcohol mixture for 3 hours. Additive – 2-o-hydroxyphenylbenzoxazole	0.01	215	400	4	350	610	433
6	Film treated with Chlorex-alcohol mixture (2:3) for 18 hours. Additive – diethyl dihydroxyterephthalate	0.004	13	309	6	292	51***	275
7	Film treated with Chlorex-alcohol mixture (2:3) for 18 hours. Additive – 2-o-hydroxyphenylbenzoxazole	0.004	46	1005	12.1	635	60	934
8	Film treated with Chlorex-alcohol mixture (2:3) for 18 hours. Additive – salol	0.004	27	701	23	650	62	830
9	Film treated with Chlorex-alcohol mixture (2:3) for 18 hours. Additive – β-methylumbelliferone	0.004	34	983	3.5	648	19	862

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*Elongation rate of Samples 1-5 was 0.073 mm/sec, of Samples 6-9 – 0.008 mm/sec.

**Exposure time for Samples 1-5 was 50 hours, for Samples 6-9 – 100 hours.

***This sample elongated at a rate of 0.072 mm/sec.

2-o-Hydroxyphenylbenzoxazole displayed some protective action (see Table). It should be pointed out that this compound had little effect on the photochemical degradation of polystyrene, contributing only to the process of structure formation [7] (Fig. 5).

Diethyl dihydroxyterephthalate displayed a slight sensitizing effect on the course of the photochemical degradation of polyethylene terephthalate (Fig. 6). Just as in the preceding communication, we attribute this effect to the absence of absorption in the region of 250-320 mμ by diethyl dihydroxyterephthalate This is apparently also the chief reason that diethyl dihydroxyterephthalate has no inhibiting properties and is incapable of slowing down the photochemical degradation of polyethylene terephthalate.

For their aid in the recording of the absorption spectra and in the determination of the mechanical properties, the authors express their deep appreciation to I.V. Obreimov, G.L. Slonimskii, I.Ia. Kachkurova, L.Z. Rogovina and T.A. Dikareva.

SUMMARY

1. The degradation of polyethylene terephthalate under the influence of ultraviolet irradiation was investigated.

2. It was found that degradation of polyethylene terephthalate proceeds considerably more intensely under the influence of the total ultraviolet radiation from a PRK-2 lamp than under the influence of light with a wavelength of 300-320 mμ.

3. The introduction into polyethylene terephthalate of low-molecular-weight organic compounds as additives has an effect on the degradation of the polyester.

4. The results are in agreement with the results obtained in the investigation of the effect of these same additives on the course of the degradation of polystyrene.

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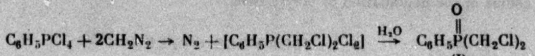
*Original Russian pagination. See C.B. translation.

THE INTERACTION OF PHENYLPHOSPHORUS TETRACHLORIDE WITH DIAZOMETHANE

L.M. Iagupol'skii and P.A. Iufa

The reaction of aliphatic diazo compounds with phosphorus halogen compounds has been studied by Iakubovich and Ginsburg [1]. They showed that phosphorus trichloride and pentachloride react with diazomethane at temperatures of −60 to −40°. In the case of phosphorus trichloride, the reaction stops at the stage of the monoalkyl derivative – chloromethylphosphorus dichloride is formed; with phosphorus pentachloride, the reaction proceeds to the trialkyl derivative – trichlorotrimethylphosphine is formed.

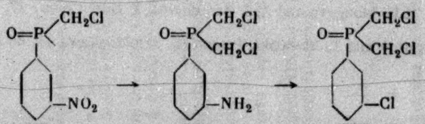
It was of interest to investigate the reaction of arylphosphorus tetrachloride with diazomethane. It was found that phenylphosphorus tetrachloride reacts very readily with diazomethane at −40°. Hydrolysis of the product gave ω,ω'-dichlorodimethylphenylphosphine oxide. The reaction apparently proceeds through a stage in which the readily hydrolyzable ω,ω'-dichlorodimethylphenyl dichloride is formed.



$$C_6H_5PCl_4 + 2CH_2N_2 \rightarrow N_2 + [C_6H_5P(CH_2Cl)_2Cl_2] \xrightarrow{H_2O} C_6H_5\overset{\overset{O}{\|}}{P}(CH_2Cl)_2$$

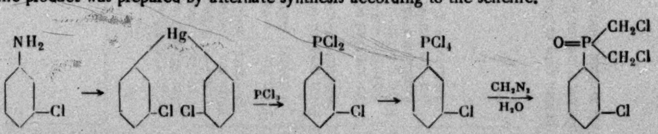
(I)

The dichlorodimethylphenylphosphine oxide (I) was in the form of colorless prisms. It was readily soluble in alcohol and acetone, difficultly soluble in benzene, and sparingly soluble in water. The chlorine atoms in the chloromethyl groups enter into exchange reactions only with difficulty. They can be replaced by iodine by means of potassium iodide, but only under rigorous conditions – in boiling glycol. The nitration of (I) can be carried out by heating with the nitrating mixture on a boiling-water bath. The nitro group enters the meta position. This was proved as follows. The nitro group was reduced to an amino group, and the latter was replaced with chlorine by the Sandmeyer reaction.

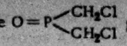


(II) (III) (IV)

This same product was prepared by alternate synthesis according to the scheme:



A mixture of these substances showed no depression of the melting point.

Therefore, the  $O{=}P\begin{smallmatrix}CH_2Cl\\CH_2Cl\end{smallmatrix}$ group is meta orienting.

EXPERIMENTAL

ω ω'-Dichlorodimethylphenylphosphine oxide (I). 150 ml of absolute ether and 25 g (0.1 mole) of phenylphosphorus tetrachloride [2], prepared from phenyldichlorophosphine [3] and chlorine, were charged to a reactor fitted with a stirrer, a dropping funnel, a thermometer, and a condenser connected to a calcium chloride tube. The mixture was cooled to −40°, and at this temperature, a solution of 9.7 g (0.23 mole) of diazomethane in 300 ml of ether was added over the course of an hour; the diazomethane solution was precooled to −2° and dried successively over KOH and sodium wire. After the addition of half of the diazomethane solution, a colorless sludge formed. At the conclusion of the addition of the diazomethane, stirring was continued for 30 minutes at a temperature of −40 to −35°, and then the reaction mixture was allowed to stand overnight at 0°. On the following day, without separating the sludge, the ether was distilled on a water bath, and the residue was added to 500 ml of water. Foaming occurred and heat was evolved during the addition. After a day, the product was suction filtered, washed with water, dried, and crystallized from methyl alcohol. The yield was 7.0 g (31.4%). M.p. 141-142°.

Found %: Cl 32.13, 32.31. $C_8H_9OPCl_2$. Calculated %: Cl 31.83.

ω,ω'-Dichlorodimethyl-(m-nitrophenyl)phosphine (II). The nitrating mixture [9.9 g of HNO_3 (d 1.5) and 16.1 g of H_2SO_4 (d 1.83)] was placed in a flask with a ground-glass joint, cooled to 0°, and, with stirring, 5.58 g of (I) was gradually added. A reflux condenser was joined to the flask, and the flask and contents were heated on a boiling water bath for 45 minutes. The solution was cooled and poured onto ice. The product was filtered and washed with water. Recrystallization from methyl alcohol or benzene resulted in light-yellow prisms with a m.p. of 155-156°. The yield was 6 g (93%). (II) is readily soluble in hot methyl and ethyl alcohols and benzene, but very slightly soluble in the cold solvents.

Found %: N 5.25, 5.32; Cl 26.51, 26.63. $C_8H_8O_3NPCl_2$. Calculated %: N 5.22; Cl 26.49.

ω,ω'-Dichlorodimethyl-(m-aminophenyl)phosphine oxide (III). A solution of 5.36 g (0.02 mole) of (II) in 50 ml of ethyl alcohol was placed in a reactor fitted with a stirrer, a dropping funnel, a reflux condenser, and a thermometer; the solution was heated on a water bath to 70°, and a solution of 15.9 g (0.07 mole) of $SnCl_2 \cdot 2H_2O$ in 10 ml of HCl (d 1.19) was added dropwise over a period of 30 minutes. The mixture was heated at this temperature for one hour, and then refluxed for 15 minutes. The alcohol was distilled under the vacuum of a water aspirator. An excess of 30% alkali was added to the residue. The product was extracted with ether (five times with 40-50 ml portions). The ether solution was dried, and the ether was distilled. The yellowish prisms were recrystallized from benzene. The yield was 2.33 g (56%). M.p. 110-111°. The product was readily soluble in alcohol and hot benzene and sparingly soluble in cold benzene.

Found %: N 6.10, 6.15; Cl 29.54, 29.98. $C_8H_{10}ONPCl_2$. Calculated %: N 5.88; Cl 29.82.

Prisms of the acetyl derivative were recrystallized from water; m.p. 163-164°.

Found %: N 5.13, 5.16. $C_{10}H_{12}O_2NPCl_2$. Calculated %: N 5.0.

ω,ω'-Dichlorodimethyl-(m-chlorophenyl)phosphine oxide (IV). 0.72 g (0.003 mole) of (III) was dissolved in 2 ml of 20% HCl; the solution was cooled to −3°, and diazotized with a solution of 0.22 g (0.003 mole) of sodium nitrite in 2 ml of water. A solution of 0.4 g (0.004 mole) of cuprous chloride in 3 ml of 30% hydrochloric acid was prepared, and, with vigorous stirring, the solution of diazonium salt was added to the cuprous chloride solution. The reaction proceeded violently. The mixture was allowed to stand at room temperature. On the following day, the mixture was heated at 60° for 30 minutes. The product was cooled, filtered, washed with water, and dried. White crystals were obtained by recrystallization from water. The yield was 0.4 g (52%). M.p. 129-130°. The product was readily soluble in alcohol and benzene, more difficultly soluble in hot water, and sparingly soluble in cold water.

Found %: Cl 41.65, 41.75. $C_8H_8OPCl_3$. Calculated %: Cl 41.36.

Di(m-chlorophenyl)mercury. A solution of 57 g (0.21 mole) of mercuric chloride in 75 ml of hydrochloric acid (d 1.19) was placed in a reactor fitted with a stirrer and thermometer. The solution was cooled with an ice-salt mixture, and 75 g of finely crushed ice was added. A solution of 17.5 g (0.25 mole) of sodium nitrite was added, with stirring, at a rate such that the temperature did not rise above −5°. A cooled solution of 25.5 g (0.2 mole) of m-chloroaniline in 100 ml of ether was then added rapidly. The mixture was stirred vigorously for 15 minutes, and the product was filtered and washed with water, alcohol, and ether. The yield of the double salt of chlorobenzenediazonium chloride and mercuric chloride was 70 g. 20 g (0.32 g-atom) of copper powder and 100 ml of acetone were placed in a flask fitted with a stirrer. The mixture was cooled to −5°, and 22.3 g (0.05 mole) of the double salt was added. The reaction began at 0°. Exothermic heat raised the temperature to 13°. Ten minutes after the reaction had subsided, 100 ml of 25% aqueous ammonia was added. On the following day, the mixture was refluxed for two hours and diluted with water to 700 ml. After two hours, the precipitate was filtered and washed on the filter with water and a small amount of ether. The organomercury compound was extracted from the precipitate with ether (four times with 100-ml portions). The chloroform was distilled. Silvery crystals were obtained by recrystallization from alcohol. The yield was 3.12 g (23%). M.p. 148-149°. Di-(m-chlorophenyl)mercury is readily soluble in hot benzene, chloroform, alcohol and acetone.

Found %: Cl 16.44, 16.51. $C_{12}H_8Cl_2Hg$. Calculated %: Cl 16.52.

m-Chlorophenylphosphorus dichloride. 0.5 g (0.02 mole) of di(m-chlorophenyl)mercury and 25 g (0.18 mole) of PCl_3 were sealed in a tube and heated at 230-250° for 24 hours. The tube was opened, and the liquid was rapidly filtered through a Nutsch filter. The tube and the precipitate were washed with absolute petroleum ether. The petroleum ether was distilled, and the liquid residue was distilled under vacuum. The yield was 6.8 g; b.p. 101-103° (5 mm). The liquid was filtered through a No. 4 glass filter and again vacuum distilled to remove the mercuric chloride.

m-Chlorophenylphosphorus dichloride is a liquid with a disagreeable odor; it is readily soluble in C_6H_6 and CCl_4 and less soluble in petroleum ether; it is hydrolyzed by cold water.

Found %: Cl, after hydrolysis, 33.06, 33.15. $C_6H_4PCl_3$. Calculated %: Cl, after hydrolysis, 33.26.

m-Chlorophenylphosphorus tetrachloride. 2.14 g of m-chlorophenylphosphorus dichloride was placed in a flask. Dry chlorine was passed through a tube which opened over the surface of the liquid until the theoretical amount (0.71 g) was absorbed; the flask was cooled periodically with water. Dry CO_2 was then passed into the flask. The product crystallized from solution. The melting point of the raw product was 46-47° in a sealed capillary. The yield was 2.75 g (quantitative).

Found: equiv. (after hydrolysis) 5.99. $C_6H_4PCl_5$. Calculated: equiv. 6.

ω,ω'-Dichlorodimethyl-(m-chlorophenyl)phosphine oxide. This compound was prepared by the same method as (I). From 2.8 g (0.01 mole) of m-chlorophenylphosphorous tetrachloride in 30 ml of ether and 1.1 g (0.025 mole) of diazomethane in 100 ml of ether was obtained, after crystallization from water containing carbon, 0.7 g (31%) of product with a m.p. of 129°.

ω,ω'-Diiododimethylphenylphosphine oxide. 2.23 g (0.01 mole) of (I), 4.4 g (0.026 mole) of KI, and 18 ml of glycol were placed in a flask with a ground-glass joint and fitted with a reflux condenser and calcium chloride tube; the mixture was refluxed for six hours, cooled, and poured onto ice. The product was filtered. White prisms were obtained by recrystallization from aqueous alcohol. The yield was 2.5 g (61.5%). M.p. 172-173°. The product was soluble in methyl and ethyl alcohol on heating.

Found %: I 62.50, 62.60. $C_8H_9OPI_2$. Calculated %: I 62.56.

SUMMARY

Phenylphosphorus tetrachloride reacts with diazomethane to yield ω,ω'-dichlorodimethylphenylphosphine oxide. The ω,ω'-dichlorodimethylphenylphosphine oxide group is meta orienting during electrophilic substitution in an aromatic ring.

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SYNTHESIS OF 6-BROMO-8-MERCAPTOQUINOLINE (6-BROMOTHIOOXINE) AND SOME OF ITS PROPERTIES

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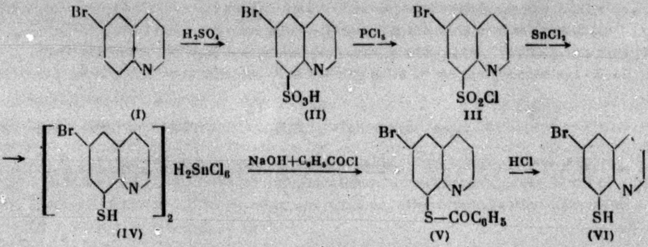
As shown by investigations currently in progress, 8-mercaptoquinoline (thiooxine) is a good analytical reagent for the colorimetric determination of metals – copper, palladium, molybdenum, manganese, vanadium, and others [1]. Derivatives of 8-mercaptoquinoline are also of interest as possible analytical reagents, since the presence of substituents on the quinoline ring could have an effect on the properties of the functional atomic groups and thereby change the analytical quality of the reagent.

The synthesis of 8-mercaptoquinoline and 5-bromo-8-mercaptoquinoline was accomplished by Edinger [2] and improved by one of us [3]. The preparation of 4-chloro-8-mercaptoquinoline was described later [4]. The preparation of 6-bromo-8-mercaptoquinoline is described in the present communication. Following the method of A. Edinger, the synthesis of 6-bromo-8-mercaptoquinoline (VI) can be represented by the following scheme:



EXPERIMENTAL

6-Bromoquinoline was prepared by the method of Skraup from p-bromoaniline [5].

Preparation of 6-bromoquinoline-8-sulfonic acid. The sulfonation of 6-bromoquinoline was carried out by the method described for the preparation of quinoline-8-sulfonic acid [6], except that the 6-bromoquinoline was first converted by the calculated amount of concentrated sulfuric acid to the sulfate. The latter was gradually added in small portions to a three-fold amount (calculated on the weight of 6-bromoquinoline) of 60% oleum. This procedure kept the evolution of heat and the loss of SO_3 to a minimum. 55 g of 6-bromoquinoline was gradually added, with stirring, to 26 g of concentrated sulfuric acid. Over a one-hour period, small portions of the solidified 6-bromoquinoline sulfate were added, with agitation, to 160 g of 60% oleum. The reaction mixture was held at 170° for five hours in a flask connected to a reflux condenser by means of a ground-glass joint. The contents of the flask were cooled, poured into 800 g of ice, and allowed to stand overnight. The 6-bromoquinoline-8-sulfonic acid was separated and washed two to three times with water; the yield was 70 g (79%).

For preparation of the sodium salt, the 6-bromoquinoline-8-sulfonic acid was suspended in 0.5 liter of water and neutralized (to a pH of about 7) by heating with a 20% solution of NaOH (the pH was determined with universal indicator paper). The solution was evaporated, and the sodium salt was dried at 160° and carefully ground.

6-Bromoquinoline-8-sulfonyl chloride. 74 g of the sodium salt of 6-bromoquinoline-8-sulfonic acid was carefully mixed with 70 g of ground phosphorus pentachloride, and the mixture was heated in a flask on an oil bath. The reaction began at a temperature of about 100°, and the mixture became liquid owing to the formation of phosphoryl chloride. The temperature of the bath was raised to 140-145°, and the reaction mixture was held at this temperature for 10-20 minutes to the beginning of solidification. Then, before the melt solidified in the flask, it was poured into a large porcelain mortar, distributed in a smooth layer, and, at the instant of setting, it was scraped from the sides of the mortar with a porcelain spatula and ground as carefully as possible. After the 6-bromoquinoline-8-sulfonyl chloride had cooled completely, 300 ml of water and ice was poured into the mortar, and grinding of the solid lumps was continued to separate out the phosphoryl chloride and to leach out the sodium chloride. After 10-15 minutes, the sulfonyl chloride was suction filtered, washed with ice water, and carefully pressed. 93 g of moist sulfonyl chloride was obtained.

Reduction of 6-bromoquinoline-8-sulfonyl chloride. The 6-bromoquinoline-8-sulfonyl chloride was reduced with stannous chloride on the same day in which it was prepared since it undergoes decomposition when moist. 210 g of $SnCl_2 \cdot 2H_2O$ (analytical grade) was dissolved in 300 ml of concentrated hydrochloric acid. The sulfonyl chloride was then dissolved in 300 ml of concentrated hydrochloric acid. This solution was prepared at the very last moment, since the sulfonyl chloride rapidly decomposes when dissolved in hydrochloric acid. The slowly dissolving lumps of 6-bromoquinoline-8-sulfonyl chloride remaining on the bottom of the flask were ground, and, without waiting for them to dissolve completely, the solution was poured in a thin stream, with stirring, into the solution of stannous chloride. When the solutions had mixed, the mixture was warmed, and a lemon-yellow crystalline precipitate of the complex of stannic chloride with 6-bromo-8-mercaptoquinoline formed. The stannic chloride salt was cooled, filtered on a Büchner funnel, washed with 50 ml of hydrochloric acid (1 : 1) and then with water, and carefully pressed. 176 g of the moist stannic chloride salt was obtained.

Decomposition of the stannic chloride complex with 6-bromomercaptoquinoline-8-sulfonyl chloride and preparation of the benzoyl derivative. To 176 g of the stannic chloride salt obtained in the preceding experiment was added, in small portions and with stirring, a solution of 50 g of NaOH in the least possible amount of water until a homogeneous mass was formed. 0.5 liter of water was added, and the mixture was brought to boiling, after which it was diluted with another 0.5 liter of water. The yellow precipitate went into solution. The dark-yellow, turbid solution was filtered. If an appreciable amount of undecomposed stannic chloride salt remained on the filter, the treatment with alkali was repeated using a more dilute solution. The dark-yellow filtrate, which gradually became turbid, was cooled, poured into a large bottle with a ground-glass stopper, and vigorously agitated with small portions (2-3 ml) of benzoyl chloride until the solution was decolorized. During this procedure, it was necessary constantly to follow the pH of the medium (by means of universal indicator paper); the medium must be strongly alkaline ($pH \approx 10$). If the pH dropped too low, 20-30 ml of a 20% solution of NaOH was added. A yellow, grainy precipitate of the benzoyl derivative of 6-bromo-8-mercaptoquinoline formed; the precipitate was filtered and washed with a dilute solution of alkali and then with water.

Decomposition of the benzoyl derivative and isolation of 6-bromo-8-mercaptoquinoline. The benzoyl derivative obtained in the preceding experiment was refluxed with 350 ml of concentrated hydrochloric acid in a 500-ml flask joined to a reflux condenser by means of a ground-glass joint. The mixture was slowly boiled, and after approximately 40-60 minutes, complete decomposition of the benzoyl derivative occurred with the formation of a transparent, dark-yellow solution. The solution was cooled over a period of 2-3 hours, and the precipitated coarse crystals of benzoic acid were filtered and washed with a small amount of hydrochloric acid (1 : 1).

The yellow filtrate (a hydrochloric acid solution of 6-bromo-8-mercaptoquinoline) was transferred to a 2-liter flask, the flask was placed in an ice bath, and the contents were neutralized (as indicated by universal indicator paper) with a saturated, carefully filtered solution of sodium carbonate (130 g of Na_2CO_3 in 300 ml of water). Dark-red crystals of 6-bromo-8-mercaptoquinoline precipitated when the pH reached 5.5-6. Occasionally, when the solution was insufficiently cooled during neutralization, the 6-bromo-8-mercaptoquinoline separated in the form of a heavy, blue oil, which crystallized after some time. The crystals were suction filtered, washed several times with water, and dried at room temperature on a sheet of filter paper. The yield was 15 g (19%). Analysis of the purified preparations indicated that the material contained two molecules of water of crystallization.

Found %: H 3.69; N 4.94; S 11.48. $C_9H_6NSBr \cdot 2H_2O$. Calculated %: H 3.62; N 5.06; S 11.58.

6-Bromo-8-mercaptoquinoline is very sparingly soluble in water (with the formation of a yellow-orange solution); it is soluble in ethyl alcohol and in ether to the extent of about 0.6 g and 10 g per 100 ml, respectively; it is soluble in other water-miscible solvents (acetone, dioxane). It is extracted from aqueous solutions by water-immiscible organic solvents. The extracts have a yellow or orange color, and the color is more intense than that of extracts of 8-mercaptoquinoline. This indicates that the water of crystallization is firmly bound in the 6-bromo-8-mercaptoquinoline, and the reagent goes into the organic solvent (at least partially) in the form of the intensely colored dihydrate.

6-Bromo-8-mercaptoquinoline dihydrate is converted at 89.5° to a blue liquid similar to anhydrous 8-mercaptoquinoline. It may be assumed that, as in the case of 8-mercaptoquinoline, melting of 6-bromo-8-mercaptoquinoline occurs with the loss of the water of crystallization and conversion to the liquid, anhydrous, blue 6-bromo-8-mercaptoquinoline. When heated in a capillary, the blue liquid condenses on the walls of the capillary in the form of blue drops which soon crystallized, forming completely colorless, acicular crystals. These crystals gradually (in the course of 30-50 minutes) added the water which had been split from the dihydrate, and were again converted to bright-red crystals of the dihydrate. We previously observed a similar phenomenon during the dehydration of 8-mercaptoquinoline dihydrate under vacuum. In this case, after some time in the evacuated desiccator, the partially dehydrated, red 8-mercaptoquinoline dihydrate was observed in the form of a white, solid mass, which, on further dehydration, was converted to a blue liquid. The white, intermediate product formed during the dehydration of 8-mercaptoquinoline is apparently unstable and is formed under strictly fixed conditions, since we did not observe it in further experiments. In the case of 6-bromo-8-mercaptoquinoline, the white intermediate product is stable, is formed readily, and can be isolated. The composition of this substance is not clear. It may be assumed that the product is the monohydrate in both cases.

As pointed out above, at 89.5° 6-bromo-8-mercaptoquinoline dihydrate is converted to a liquid, splitting off water of crystallization. Thus, 89.5° is not the melting point, but the decomposition temperature of the dihydrate. The removal of water of crystallization from 8-mercaptoquinoline takes place at 59°. The greater strength of the bonding of the water of crystallization in 6-bromo-8-mercaptoquinoline explains its significantly greater stability (as compared to 8-mercaptoquinoline) toward the action of atmospheric oxygen. 6-Bromo-8-mercaptoquinoline dihydrate was unchanged after standing open to the air for two months. In comparison, 8-mercaptoquinoline oxidized in a few days under the same conditions.

Preliminary experiments showed that, as a reagent of the type R–SH, 6-bromo-8-mercaptoquinoline interacts in aqueous solutions with cations formed from sulfides which are not hydrolyzed by water; water-insoluble inner-complex salts are formed, and these frequently impart an intense color to the organic solvents with which they are extracted. A more detailed study of the properties of these salts is under way at the present time.

SUMMARY

1. 6-Bromo-8-mercaptoquinoline, which has not been described in the literature, was synthesized; it separates from aqueous solutions in the form of the red, crystalline dihydrate. The dehydration of this substance was studied.

2. In aqueous solutions, 6-bromo-8-mercaptoquinoline forms, with the cation groups of hydrogen sulfide and ammonium sulfide, colored inner-complex salts which are insoluble in water and soluble in organic solvents.

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THE NUMBER OF OPTICAL STEREOISOMERS AND THEIR DISTRIBUTION WITH RESPECT TO THE DIFFERENT TYPES OF CONFIGURATION IN COMPOUNDS WITH CONTINUOUS SERIES OF ASYMMETRIC CENTERS IN AN UNBRANCHED CHAIN

L.A. Mai

The question of the number of optical stereoisomers and their distribution with respect to the different types of configuration is of great interest in the chemistry of sugars and other compounds with a continuous series of asymmetric centers. Moreover, up to the present, there has been no classification of such compounds by type of configuration of the chain of asymmetric centers, and the distribution of the stereoisomers with respect to the various types of configuration is unknown. Formulas for the calculation of the number of stereoisomers have been presented by Van't Hoff [1] and by E. Fischer [2] for simple cases of compounds with few asymmetric centers in an unbranched chain and by Senior [3] for certain more complex cases with a branched chain. A general method for calculating the number of optical and geometrical stereoisomers was developed by Branch and Hill [4].

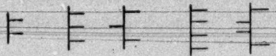
In the present communication we shall consider the distribution of optical stereoisomers with respect to the various configurational types in compounds having the structure $X(CHZ)_nY$, where X, Y and Z are groups which do not contain asymmetric centers. Sugars and their α,ω-derivatives are examples of compounds of this type. We divide compounds of this type into three groups according to the steric configuration of the chain of asymmetric centers (configurational symmetry of the chain) regardless of whether they have like or unlike terminal groups X and Y.

1) Symmetrical type – the molecule has a plane of symmetry; this type is possible for any (even or uneven) value of n (erythro-, xylo-, ribo-, allo-, gala-configuration) (A).

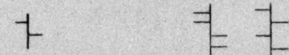
2) Antisymmetric ("quasi-centrosymmetric") type – rotation of one half of the molecule through 180° leads to a position of mirror symmetry with respect to the second half of the molecule; this type is possible only for an even number of carbon atoms n (threo-, manno-, ido-configuration) (B).

3) Unsymmetrical type – the molecule has no plane of symmetry, and also does not conform to the condition for an antisymmetric type; this type is possible with any value of n (starting with 3) (arabo-, lyco-, altro-, talo-, gluco-, gulo-configuration) (C).

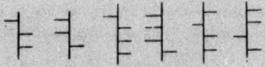
As an example we may cite the polyoxymethylene chain (one enantiomorphous stereoisomer) of tetroses, pentoses and hexoses.



A



B



C

Compounds with like terminal groups, X and Y, we shall call homoterminal, while those with unlike terminal groups we shall call heteroterminal. The ratio of the number of, and the configurational interconnection of, homoterminal and heteroterminal stereoisomers having the same chain of asymmetric centers are characteristics of each of the above types of configuration. Each symmetric homoterminal compound corresponds to two enantiomorphous stereoisomeric (D,L) heteroterminal compounds, each antisymmetric homoterminal compound corresponds to one heteroterminal compound with the same steric configuration, and each unsymmetrical homoterminal compound corresponds to two heteroterminal diasteroisomers. In the sugar group, these relationships were established chiefly by the classic researches of E. Fischer and G. Kiliani, and, as is well known, constitute the basis of one of the most important routes for determining steric configuration, namely, oxidation-reduction conversion of aldoses into the corresponding sugar alcohols and α,ω-dicarboxylic acids.

1) On oxidation of one of the terminal groups, a symmetrical sugar alcohol gives an aldose racemate, and a dicarboxylic acid forms the monolactone racemate, for example, in the conversion cycle dulcitol – D,L-galactose – mucic acid – D,L-monolactone of mucic acid – D,L-galactonic acid – D,L-galactose – dulcitol.

2) On going from antisymmetric sugar alcohols to the corresponding aldose and α,ω-dicarboxylic acid, the configuration of the chain is retained; for example, D-mannitol – D-mannose – D-mannosaccharic acid – (dilactone of D-mannosaccharic acid) – D-mannitol.

3) An unsymmetrical sugar alcohol and α,ω-dicarboxylic acid correspond to two diastereoisomeric aldoses, monolactones, and aldonic acids; for example, D-sorbitol – D-glucose, L-glucose – D-glucosaccharic acid – 2 diastereoisomeric monolactones – D-gluconic acid, L-gluconic acid – D-glucose, L-glucose – D-sorbitol.

Formulas for calculating the number of optical stereoisomers can be derived as follows. If the molecule has *n* asymmetric centers (regions) (*a*, *b*, *c* . . . *n*) with the possibilities (possible number of stereoisomers) p_a, p_b, p_c . . . p_n, then the total number of stereoisomers for the given molecule is

$$N = p_a \cdot p_b \cdot p_c \cdots p_n. \tag{1}$$

Since in the case of optical stereoisomers, each asymmetric center (region) has two possibilities ($p_a = p_b = \ldots = 2$),

$$N = 2^n. \tag{2}$$

This formula, however, holds only in the case of *n* structurally different asymmetric regions; i.e., it gives the number of heteroterminal stereoisomers. In case there are present structurally equivalent asymmetric regions (according to the conditions for configurational symmetry presented above), the number of stereoisomers is given by the formula

$$N = 2^{n-\nu}, \tag{3}$$

where ν is the number of equivalent asymmetric centers. According to the conditions of classification of configurational symmetry, for heteroterminal-symmetric compounds with an even value of *n*, $\nu = n/2$, with odd values of *n*, $\nu = (n-1)/2$, and for antisymmetric compounds, $\nu = n/2$. By the introduction of the trigonometric multipliers $\sin^2(\pi n/2)$ and $\cos^2(\pi n/2)$, we can express the total number of stereoisomers for even and odd values of *n* by equations for the number of symmetric (N_s) and antisymmetric (N_a) stereoisomers. The difference $N - N_s - N_a$ gives the number of unsymmetrical stereoisomers, N_u.

Owing to the possibility of inversion identity ("head-tail" rotation), the total number of homoterminal stereoisomers is less than the number of the corresponding heteroterminal compounds; for odd values of *n*

$$N' = \frac{2^n}{2} = 2^{n-1}, \tag{4}$$

and for even values of *n*, this number is increased by the number of antisymmetric stereoisomers for which inversion identity does not exist (for example, D- and L-mannosaccharic acids)

$$N' = \frac{2^n}{2} + \frac{2^{\frac{n}{2}}}{2} = \frac{2^n + 2^{\frac{n}{2}}}{2}. \tag{5}$$

For individual types of configurational symmetry (N_s', N_a'), the values of ν [Formula (3)] are obtained in the same manner as for heteroterminal compounds, from the classification conditions of symmetry. The number of unsymmetrical stereoisomers N_u is similarly obtained from the difference $N' - N_c' - N_a'$. All of the formulas presented below can also be derived by calculating the possibilities for a region and successively combining antisymmetric regions according to the general method of Branch and Hill [4].

Using a single function for any value of n instead of separate functions for even and odd values of n, the number of stereoisomers (without accounting for racemic, anomeric, and other forms) can be expressed by the following equations.

The Number of Stereoisomers and Their Distribution According to Type of Configuration for $X(CHZ)_nY$ Compounds

No. of asymmetric C atoms (n)	Heteroterminal compounds (X ≠ Y)				Homoterminal compounds (X = Y)			
	symmetrical	antisymmetric	unsymmetrical	total	symmetrical	antisymmetric	unsymmetrical	total
1	(2)	0	0	2	1	0	0	1
2	2	2	0	4	1	2	0	3
3	4	0	4	8	2	0	2	4
4	4	4	8	16	2	4	4	10
5	8	0	24	32	4	0	12	16
6	8	8	48	64	4	8	24	36
7	16	0	112	128	8	0	56	64
8	16	16	224	256	8	16	112	136
9	32	0	480	512	16	0	240	256
10	32	32	960	1024	16	32	480	528

I. Heteroterminal Compounds

1) Total number of stereoisomers

$$N = 2^n. \qquad (2)$$

2) Number of symmetrical stereoisomers

$$N_c = 2^{\frac{n+\sin^2\frac{\pi n}{2}}{2}}. \qquad (6)$$

3) Number of antisymmetric stereoisomers

$$N_a = 2^{\frac{n}{2}} \cos^2\frac{\pi n}{2}. \qquad (7)$$

4) Number of unsymmetrical stereoisomers

$$N_{н} = 2^n - 2^{\frac{n}{2}}\left(\cos^2\frac{\pi n}{2} + 2^{\frac{1}{2}\sin^2\frac{\pi n}{2}}\right). \qquad (8)$$

II. Homoterminal Compounds

1) Total number of stereoisomers

$$N' = \frac{N}{2}\left(1 + \frac{1}{\sqrt{2^n}}\cos^2\frac{\pi n}{2}\right) = 2^{n-1} + 2^{\frac{n-2}{2}}\cos^2\frac{\pi n}{2}. \qquad (9)$$

2) Number of symmetrical stereoisomers (they are all diastereoisomers)

$$N_c' = \frac{N_c}{2} = 2^{\frac{n+\sin^2\frac{\pi n}{2}-2}{2}}. \qquad (10)$$

3) Number of antisymmetric stereoisomers

$$N_a' = N_a = 2^{\frac{n}{2}}\cos^2\frac{\pi n}{2}, \qquad (11)$$

i.e., $2^{(n-2)/2}\cos^2(\pi n/2)$ are enantiomorphous pairs.

4) Number of unsymmetrical stereoisomers

$$N'_н=\frac{N_н}{2}=2^{n-1}-2^{\frac{n-2}{2}}\left(\cos^2\frac{\pi n}{2}+2^{\frac{1}{2}\sin^2\frac{\pi n}{2}}\right). \quad (12)$$

In the Table are presented the numbers of possible stereoisomers for a given number of asymmetric carbon atoms up to 10, and also their distribution according to type of configuration.

SUMMARY

1. Classifications and characteristics of types of configuration (configurational symmetry) are given for compounds with continuous series of asymmetric centers in an unbranched chain.

2. Equations are given for calculating the number of optical stereoisomers of all three types; in place of different functions for even and uneven values of the variable (number of asymmetric centers), single functions are derived for any value of the variable, and these exhibit the oscillating character of the given dependence.

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REACTIONS OF PYRIDINIUM SALTS

II. INTERACTION OF CHLORO-2,4-DINITROPHENYLATES OF SUBSTITUTED PYRIDINE BASES WITH ANILINE

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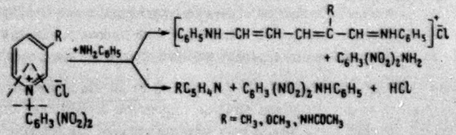
In spite of the long time that reactions resulting in the opening of the pyridine ring have been known, the effect of substituents in the pyridine ring on the course of this reaction has remained obscure up to the present. In connection with this, we have undertaken an investigation of the interaction of the chloro-2,4-dinitrophenylate of pyridine [N-(2,4-dinitrophenyl)pyridinium chloride] and its derivatives (cf. [1, 2]) with aromatic amines, particularly with aniline. It was found that this reaction can proceed in different directions depending on the nature of the substituents, its position in the pyridine ring, and the temperature conditions. When a weakly electropositive substituent (for example, CH_3, $NHCOCH_3$) is present in the β-position, cleavage of the pyridine ring proceeds at 0-15° (in ethyl alcohol medium), but the yield is less than in the case of unsubstituted pyridine. When alcoholic solutions of such chlorodinitrophenylates are heated with aniline, the formation of 2,4-dinitrodiphenylamine takes place along with ring cleavage. In the latter case, rupture of the $N-C_6H_3(NO_2)_2$ bond evidently proceeds under the action of the amine. Picrates of the corresponding pyridine bases were isolated from the reaction solutions of the individual experiments.

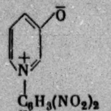

R
$+NH_2C_6H_5$
Cl
$C_6H_3(NO_2)_2$
$[C_6H_5NH-CH=CH-CH=C(R)-CH=NHC_6H_5]^+Cl^-$
$+ C_6H_3(NO_2)_2NH_2$
$RC_5H_4N + C_6H_3(NO_2)_2NHC_6H_5 + HCl$
$R = CH_3, OCH_3, NHCOCH_3$

It should be pointed out that in the case of the chlorodinitrophenylate of β-picoline [N-(dinitrophenyl)picolinium chloride], the formation of phenyldinitrophenylamine also occurs at a temperature of +5°.

Pyridine chlorodinitrophenylate is almost quantitatively cleaved by aniline in alcoholic solution, both in the cold and on heating, with the formation of the hydrochloride of the dianil of glutaconic aldehyde [3]. The conclusion follows, therefore, that the pyridine ring is stabilized by the introduction of a weakly electropositive substituent (CH_3, OCH_3 and $NHCOCH_3$ groups) into the β-position. Since the introduction of these substituents leads only to partial stabilization of the ring (along with the phenyldinitrophenylamine, some cleavage products are formed), we undertook the task of determining the effect of substituents possessing clearly expressed basic properties, for example, the dimethylamino group.

It was found that the pyridine ring in the chlorodinitrophenylate of β-dimethylaminopyridine [N-dinitrophenyl-β-dimethylaminopyridinium chloride] is very stable toward the action of aniline. This compound does not react appreciably with aniline at 0-10°, while at 60-80°, only the extra-ring nitrogen-carbon bond is cleaved. The yield of phenyldinitrophenylamine in this reaction amounts to 85% after just a three-hour heating.

The chlorodinitrophenylates of β-amino- (cf. [4]) and β-hydroxypyridine react with aniline in a manner similar to that of β-dimethylaminopyridine chlorodinitrophenylate. In the case of the hydroxy compound, the stabilizing effect on the ring bonds is undoubtedly due to the formation of the betaine (I) (cf. [1, 2]).



(I)

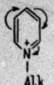
Thus, a further increase in the electropositive properties of a substituent in the β-position leads to a considerable strengthening of the ring carbon-nitrogen bonds in reactions with aromatic amines. In this case, only rupture of the extra-ring bond occurs.

A shift of a weakly electropositive substituent from the β- to the γ-position also leads to strengthening of the ring bonds. Thus, for example, in γ-acetamidopyridine chlorodinitrophenylate, in contrast to the β-derivative, the pyridine ring is cleaved neither in the cold nor by heating. In this case, only phenyldinitrophenylamine is formed (yield 11.5% after heating for three hours on a water bath). γ-Phenylaminopyridine chlorodinitrophenylate reacts in precisely the same way when heated with aniline, forming phenyldinitrophenylamine (yield 23% after heating for five hours on a water bath).

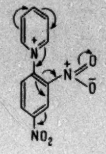
It is interesting that when an iodine atom, which possesses weakly electronegative properties, is introduced into the β-position of the pyridine ring, the stabilizing effect on the ring bonds completely disappears; β-iodopyridine chlorodinitrophenylate reacts with aniline in alcoholic solution with rupture of the ring bonds [5]. In this case, it was not possible to detect the formation of phenyldinitrophenylamine either in the cold or with heating.

On heating, the reaction of the chlorodinitrophenylates of γ-acetamido- and γ-phenylaminopyridine with aniline is accompanied by the formation of colored substances in addition to the phenyldinitrophenylamine. These same compounds are obtained when the reaction mixture is not heated. An investigation of these substances showed that they are molecular compounds. They will be described in more detail later.

Furthermore, the formation of phenyldinitrophenylamine (~2% of theoretical), in addition to products of ring cleavage, was also observed during the interaction of pyridine chlorodinitrophenylate with aniline in aqueous alcoholic solution, but not in alcoholic solution. Hence, it particularly follows that, in addition to other factors, the nature of the solvent has an effect on the course of the reaction.



(II)



(III)

It may be assumed that in the pyridinium cation (owing to the high mobility of the π-electrons of the ring), the positive charge is associated not only with the ring nitrogen atom, but also partially with the carbon atoms of the pyridine ring. Many transformations of pyridinium and quinolinium salts can be explained if it is assumed that the positive charge of their cations is delocalized, chiefly at the expense of the α- and γ-carbons of the ring (see Formula II). Thus, for example, the ready transition of N-alkyl-pyridinium and N-alkylquinolinium salts to pseudobases during their interaction with hydroxyl ions is apparently connected with the presence of a partial positive charge on the α-carbons of the cation.

When the alkyl group in N-alkylpyridinium salts is replaced by an electronegative radical, there must be a considerable shift of the π-electron density of the pyridine ring in the direction of this radical (cf., for example, Formula III). As a consequence of this, there should be a strengthening of the positive charges at the α- and α'-carbons (owing to which an attack by a nucleophilic reagent is facilitated) and a weakening of the ring C–N bonds in reactions with bases. This conclusion is in agreement with the known experimental material: alkylpyridinium and arylpyridinium halides do not react with aromatic amines in contrast to, for example, 2,4-dinitrophenylpyridinium salts (cf. [6]).

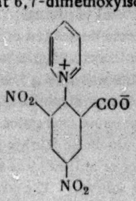
Generally speaking, the introduction of a nitro group into the benzene ring of an N-arylpyridinium salt (in a position ortho or para to the pyridine nitrogen) must lead to a weakening, not only of the ring, but also of the extra-ring C–N bonds. Experiment shows that in the case of an unsubstituted pyridine ring, the ring C–N bonds are the most vulnerable, since the attack of a nucleophilic reagent (an amine) is directed first of all at these bonds. In the pyridine chlorodinitrophenylates having electronegative substituents in the β- or the γ-positions, the π-electron density in the pyridine ring must be increased under the influence of these substituents (in comparison with derivatives which are not substituted in the ring). For this reason, an attack by an amine is directed predominantly at the extra-ring nitrogen-carbon bond rather than at the ring bonds.

From this point of view, the introduction into the pyridine ring of strongly electropositive substituents should entirely, or almost entirely, prevent the ring-cleavage reaction. As already pointed out above, experiments have confirmed this proposition. The existence of a shift of π-electrons toward the ring nitrogen atom with the introduction of electropositive substituents into the pyridine ring can, in certain cases, be confirmed indirectly – by a comparison of the experimental dipole moments with those calculated on the basis of additivity for the original bases. Thus, for example, for γ-phenylaminopyridine the experimental value of the dipole moment (3.64 D) differs considerably from the calculated value (2.72 D [7]). Such an increase can be explained only by a shift of electrons from the phenylamino group to the ring nitrogen.

The presence of color in γ-phenylaminopyridine chlorodinitrophenylate indicates a partial transition of the phenylamino group in this compound to the tetravalent state.

The conversions of chlorodinitrophenylates of β- and γ-substituted pyridines under the influence of aniline, which were the subject of our studies, constitute an example of the general reaction in which quaternary salts of pyridine, quinoline, and isoquinoline are cleaved by the action of water, alcohols, aromatic amines, phenols, and other substances. In all of these cases, rupture of the extra-ring bond proceeds especially readily if the hetero ring has little tendency toward rupture (for example, in quinoline) and if the heterocyclic nitrogen atom is joined to an electronegative radical. Thus, the presence of an electronegative radical leads, in general, not only to a weakening of the ring C−N bonds, but also to a weakening of the extra-ring N−C.

A considerable number of reactions of this nature are described in the literature. Thus, during the interaction of isoquinoline chloro-2,4-dinitrophenylate in alcoholic solution with aniline or with p-toluidine, 2,4-dinitro-α-naphthylamine and 2,4-dinitro-α-naphthyl-p-tolylamine are formed [8]. Kabachnik and Zitser found that 6,7-dimethoxyisoquinoline chloro-2,4-dinitrophenylate reacts, in alcoholic solution, with these same amines in a similar manner [9]. It is interesting that 4-pyridylpyridinium dichloride reacts with aniline to form the hydrochloride of glutaconic aldehyde dianil [glutacondianil] and γ-phenylaminopyridine [10]. Consequently, in this case, both reactions − ring cleavage and splitting off of the extra-ring radical − proceed at commensurate rates. Under the action of potassium phenolate in phenol solution, 4-pyridylpyridinium dichloride is cleaved with the formation of γ-phenoxypyridine [11]. β-Nitro-γ-pyridylpyridinium chloride is readily cleaved by water with the formation of β-nitro-γ-hydroxypyridine [12]. On heating the betaine (IV) with methyl or ethyl alcohol, rupture of the extra-ring bond occurs, and the corresponding esters of dinitrosalicylic acid and pyridine are obtained [13].



(IV)

It is interesting that in quaternary salts of aromatic amines with an electronegative radical at the nitrogen atom, rupture of the N−C bond accompanied by splitting out of alkyl halide very frequently proceeds spontaneously at ordinary temperatures. Thus, for example, the product of the addition of phosgene to trimethylamine decomposes with the evolution of methyl chloride at ordinary temperatures [14]. In precisely the same manner, the interaction of 2,4-dinitrochlorobenzene with trimethylamine readily yields 2,4-dinitrodimethylaniline with the elimination of methyl chloride [15]. The chlorodinitrophenylate of trimethylamine [dinitrophenyltrimethylammonium chloride] is so unstable that it cannot be isolated from the reaction mixture. Undoubtedly, von Braun cleavage of amines by means of cyanogen bromide also belongs to this series of reactions.

An interesting question arises as to the mechanism of the rupture of ring and extra-ring C−N bonds in pyridinium salts, particularly in the chlorodinitrophenylates of substituted pyridines, under the influence of aromatic amines and other substances. It is very probable that cleavage of these bonds proceeds simultaneously with the formation of the covalent bond between the α-carbon of the pyridine ring or the corresponding carbon of the benzene ring and the nitrogen atom in the amine molecule (cf. [16]). However, with respect to cleavage of the extra-ring bonds, another mechanism is possible. Undoubtedly, pyridine chlorodinitrophenylate and related compounds possess the dual character of quaternary ammonium salts and molecular compounds (cf., for example,[17]). However, the phenomenon of dissociation in solutions is a characteristic of many molecular compounds. As a result of an investigation of the kinetics of the reaction between picryl chloride and pyridine in ethyl alcohol, Hodges [18] came to the conclusion that the following equilibrium is established in alcohol solution:

$$C_5H_5N + ClC_6H_2(NO_2)_3 \rightleftarrows C_5H_5\overset{+}{N}C_6H_2(NO_2)_3Cl$$

It is possible that a similar equilibrium is established in alcoholic solutions of chlorodinitrophenylates of substituted pyridines.

If a chlorodinitrophenylate is insignificantly dissociated in alcoholic solution at low temperatures, and if the substituent in the pyridine ring does not possess a highly stabilizing effect on the ring bonds, then it is possible for the ring-cleavage reaction to proceed preferentially in the presence of an aromatic amine. Naturally, on heating an alcoholic solution of the chlorodinitrophenylate, dissociation will increase. In this case, when an electropositive substituent is present on the pyridine ring, the formation of phenyldinitrophenylamine (or its derivative) can emerge as the chief reaction. As already pointed out, when a weakly electropositive substituent is present in the β-position of the pyridine ring, cleavage of the extra-ring bond in the corresponding chlorodinitrophenylate proceeds (in alcoholic solutions) as the predominant reaction at elevated temperatures. Moreover, in contrast to reactions involving cleavage of the ring C–N bonds (under the influence of aromatic amines) in these same compounds, rupture of the extra-ring bond proceeds significantly more slowly. In addition, it is known that the formation of dinitro-α-naphthylphenylamine or dinitro-α-naphthyl-p-tolylamine during the action of the appropriate amines on isoquinoline chlorodinitronaphthylate [N-dinitronaphthylisoquinolinium chloride] also proceeds appreciably more slowly than the usual reaction of cleavage of the pyridine ring* (cf. [8]). All of the above statements support the assumption of the dissociation of chlorodinitrophenylates of substituted pyridines into the components during their interaction with aromatic amines in alcoholic solutions.

EXPERIMENTAL

Interaction of pyridine chloro-2,4-dinitrophenylate and aniline on heating. To a hot solution of 2.8 g of pyridine chloro-2,4-dinitrophenylate in 30 ml of 30% ethyl alcohol was added 1.86 g of aniline, and the mixture was refluxed for four hours. When the liquid was gradually cooled, a heterogeneous precipitate – yellow plates (which constituted the major part of the precipitate) and orange crystals – separated. The crystals were filtered and dried (weight, 1.65 g; m.p. 171°), and were then treated with hot toluene (twice with 5-ml portions). The insoluble portion (1.33 g) consisted of yellow plates with m.p. 179-180°, and they did not cause depression of the melting point when mixed with known 2,4-dinitroaniline. Yellow crystals of 2,4-dinitroaniline (0.06 g; m.p. 177-178°) precipitated from the cooled toluene extract. Thus, the over-all yield of dinitroaniline was 1.39 g (76%). The toluene solution was evaporated to dryness, and the residue was recrystallized from aqueous alcohol. This procedure yielded reddish-orange needles (0.02 g) with an m.p. of 156-157°, which did not cause depression of the melting point when mixed with known phenyl-2,4-dinitrophenylamine. The aqueous-alcoholic filtrate from the reaction mixture was evaporated. The residue (a viscous, dark-red liquid with the odor of aniline) was washed with toluene and dissolved in ethyl alcohol (8 ml). The picrate was precipitated from the solution. The weight of picrate was 2.94 g (76.6% calculated as the pyridine N-phenylpicrate). The picrate was in the form of fine, light-yellow needles, m.p. 122-123° (from ethyl alcohol) (123-124° [19]).

Reaction of β-picoline chloro-2,4-dinitrophenylate with aniline. a) At 5°. 0.89 g of β-picoline chloro-2,4-dinitrophenylate and 0.56 g of aniline were dissolved in 7 ml of ethyl alcohol. The dark-red liquid was allowed to stand, protected from the light, for 70 hours at 5°. The precipitated red crystals were washed on the filter with ethyl alcohol (1 ml), dried, and heated on a water bath with dry acetone (4 ml). The acetone solution was filtered, and the crystals were washed on the filter with dry acetone (2 ml). The yield was 0.27 g (29.6% calculated as the hydrochloride of α-methylglutaconic aldehyde dianil). The m.p. was 137-138° (with decomposition). (The m.p. was unchanged after recrystallization from ethyl alcohol.) The fine, bright-red needles, which were soluble in methyl and ethyl alcohol and insoluble in water, acetone, and ether, contained water of crystallization.

Found %: H_2O 1.97; N 9.04, 9.01. $C_{18}H_{19}N_2Cl \cdot 1/3H_2O$. Calculated %: H_2O 1.97; N 9.20.

The acetone filtrate was evaporated. The orange-yellow residue (weight, 0.10 g) was treated with hot toluene (12 ml). The insoluble residue was composed of orange-yellow crystals (weight, 0.04 g; m.p. 158-167°). After recrystallization from ethyl alcohol, there was obtained 0.03 g of yellow prisms with an m.p. of 178°; a mixture of these prisms with 2,4-dinitroaniline showed no depression of the melting point.

The toluene solution was agitated with 2% sulfuric acid, and was then washed with water and dried over sodium sulfate. The toluene was distilled under vacuum. The residue (0.05 g; m.p. 127-132°) was recrystallized from ethyl alcohol (2.5 ml). The resulting orange needles (0.025 g), with an m.p. of 152-153°, caused no depression of the melting point when mixed with phenyl-2,4-dinitrophenylamine.

The solution from the reaction mixture (strong odor of β-picoline!), after separation of the crystals, was evaporated at 15-20° under vacuum. The residue was washed in several portions with hot, dry acetone (28 ml). The rose crystals (0.48 g; m.p. 188-189°) did not dissolve; shaking an aqueous solution of the crystals with activated carbon, evaporation of the solution, and recrystallization of the residue from anhydrous alcohol gave a colorless substance with an m.p. of 200-201°; a mixture of this material with β-picoline chlorodinitrophenylate showed no depression of the melting point. The acetone solution was evaporated, and the residue (0.59 g) was ground, in several portions, with warm toluene (30 ml). The toluene solution was washed with 2% sulfuric acid and then with water; the solution was then dried over sodium sulfate, and the toluene was distilled under vacuum to a volume of 8-10 ml. The precipitated yellow crystals were filtered; the weight was 0.05 g; m.p. 177°; a mixture of this material with 2,4-dinitroaniline showed no depression of the melting point. The filtrate was evaporated; the residue was composed of orange-yellow crystals (0.09 g; m.p. 128-137°). Recrystallization from ethyl alcohol (4.5 ml) gave orange needles (0.04 g) with an m.p. of 152-153°; after a second recrystallization, the m.p. was 155°. A mixture of this material with phenyl-2,4-dinitrophenylamine showed no depression of the melting point. The over-all yield of crystallized phenyl-2,4-dinitrophenylamine was 0.065 g (8.3%).

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*Should be isoquinoline ring. See T. Zincke and F. Krollpfeifer, C.A., 9, 1462 (1915).

b) With heating. 0.89 g of β-picoline chloro-2,4-dinitrophenylate and 0.56 g of aniline were dissolved in 6 ml of ethyl alcohol and refluxed on a water bath (4.5 hours). The mixture of yellow prisms and orange needles which precipitated from the cooled, dark-red solution was washed on the filter with ethyl alcohol (1 ml). The weight was 0.53 g. The coarse, yellow prisms were separated mechanically (0.08 g); m.p. 166-168°. Recrystallization from 2 ml of ethyl alcohol gave 0.06 g of a substance with an m.p. of 176-178°. A mixture of this material with 2,4-dinitroaniline showed no depression of the melting point. The major part of the precipitate (0.45 g; m.p. 124-125°), which remained after separation of the yellow prisms, was recrystallized twice from anhydrous alcohol. 0.19 g of long, reddish-orange needles with an m.p. of 156-157° was obtained; a mixture of this material with phenyl-2,4-dinitrophenylamine showed no depression of the melting point. The mother liquor was evaporated, and the residue was washed with warm toluene (20 ml). The insoluble part (yellow crystals, 0.16 g, m.p. 152-165°) was recrystallized from alcohol. There was obtained 0.12 g of a substance with an m.p. of 179-180°; a mixture of this material with 2,4-dinitroaniline showed no depression of the melting point. Thus, the over-all yield of crystallized dinitroaniline was 0.18 g (33.3%).

The toluene solution was washed with dilute hydrochloric acid and then with water, and was dried over sodium sulfate. The toluene was distilled under vacuum. The residue (yellowish-orange crystals, 0.09 g, m.p. 130-138°) was recrystallized from anhydrous alcohol (1.5 ml). The yield was 0.05 g. The orange needles, m.p. 154-156°, caused no depression of the melting point when mixed with known phenyl-2,4-dinitrophenylamine. The over-all yield of crystallized phenyldinitrophenylamine was 0.24 g (30.7%).

Interaction of β-acetamidopyridine chloro-2,4-dinitrophenylate [N-2,4-dinitrophenyl-β-acetamidopyridinium chloride] with aniline. a) At 10-15°. Aniline (1.86 g) was added to a solution of β-acetamidopyridine chloro-2,4-dinitrophenylate (1.69 g) in ethyl alcohol (70 ml), and the mixture was allowed to stand at 10-15° for 24 hours. Long, thin, red crytals, which were agglomerated in groups, were separated from the dark-red liquid. They were washed on the filter with ethyl alcohol; the weight was 1.05 g, and the m.p. was 140° (with decomposition). After 24 hours, an additional 0.26 g of red needles with an m.p. of 136° (with decomposition) was separated from the filtrate from the reaction mixture. The over-all yield of the hydrochloride of α-acetamidoglutaconic aldehyde dianil was 1.31 g (76.5%). After the crystals were recrystallized from methanol, the melting point increased to 143° (with decomposition). The substance contained water of crystallization (determined by drying at 40° under vacuum).

Found %: H_2O 4.52; N 11.83, 11.86. $C_{19}H_{20}ON_3Cl \cdot H_2O$. Calculated %: H_2O 5.01; N 11.69.

We were unable to detect phenyl-2,4-dinitrophenylamine in the filtrate.

b) With heating. 1.0 g of β-acetylamidopyridine chloro-2,4-dinitrophenylate and 0.56 g of aniline were heated in a flask, fitted with a reflux condenser, in 10 ml of ethyl alcohol on a boiling water bath (four hours). From the cooled, brown-red solution, after it had stood (20 hours), was isolated a mixture (0.40 g) of brownish-red prisms and light-reddish-orange needles. The latter were separated mechanically. The weight was 0.02 g; m.p. 138-145° (after recrystallization of the material from ethyl alcohol, the m.p. increased to 156°); a mixture of this substance with phenyl-2,4-dinitrophenylamine showed no depression of the melting point. After recrystallization of the major part of the precipitate (0.38 g) from ethyl alcohol, yellow prisms of 2,4-dinitroaniline (0.27 g) were obtained; m.p. 179-180°. From the filtrate from the reaction mixture, after further standing, was isolated an additional 0.06 g of 2,4-dinitroaniline (m.p. 172-176°). The over-all yield of dinitroaniline was 0.44 g (81.3%).

Picric acid (0.68 g in 10 ml of alcohol) was added to the alcoholic filtrate after removal of the phenyl-2,4-dinitrophenylamine and 2,4-dinitroaniline. The weight of the precipitated picrate was 0.9 g (68.2% calculated as the N-phenylpicrate of β-acetamidopyridine); m.p. 142-143°. Recrystallization from alcohol gave 0.69 g of of fine, light-yellow prisms with an m.p. of 148-149°.

Found % N 15.96. $C_{19}H_{15}O_8N_5$. Calculated % N 15.86.

Reaction of β-methoxypyridine 2,4-dinitrophenylate with aniline. 0.12 g of β-methoxypyridine chloro-2,4-dinitrophenylate [N-2,4-dinitrophenyl-β-methoxypyridinium chloride] and 0.07 g of aniline were heated in 1 ml of alcohol on a water bath for 1.5 hours. Orange needles of phenyl-2,4-dinitrophenylamine, 0.38 g (38.3%), separated from the cooled reddish-brown solution. The m.p.,151-152°, increased to 156° after recrystallization of the crystals from ethyl alcohol. Dry ether was added to the filtrate. The small amount of tarry precipitate was filtered, and picric acid (0.1 g in 20 ml of ether) was added to the solution. The weight of picrate was 0.03 g (23%); m.p. 128-129° (after recrystallization from ethyl alcohol); a mixture of this material with known β-methoxypyridine picrate showed no depression of the melting point.

Reaction of β-dimethylaminopyridine chloro-2,4-dinitrophenylate with aniline. A mixture of 0.65 g of β-dimethylaminopyridine chloro-2,4-dinitrophenylate [N-2,4-dinitrophenyl-β-dimethylaminopyridinium chloride], and 0.37 g of aniline was dissolved in 4 ml of anhydrous alcohol and heated for three hours on a water bath at 60-80°. A voluminous precipitate of phenyl-2,4-dinitrophenylamine (dark-orange needles) separated from the cooled orange-brown solution. The crystals were washed on the filter with ethyl alcohol; weight, 0.4 g; m.p., 147-149°. Dark-orange needles crystallized from the filtrate on long standing; weight, 0.04 g; m.p., 146-148°. Thus, the over-all yield of phenyl-2,4-dinitrophenylamine was 0.44 g (84.9%). After recrystallization from methyl alcohol, the reddish-orange needles melted at 156-157° (weight, 0.3 g); a mixture of the crystals with known phenyl-2,4-dinitrophenylamine showed no depression of the melting point. Dry ether (150 ml) was added to the filtrate remaining after separation of the phenyl-2,4-dinitrophenylamine. The reddish-brown oil which separated was mixed with an 8% solution of sodium bicarbonate (50 ml). The dark-yellow solution was extracted with ether, and the picrate was precipitated from the ether extract; yield, 0.37 g (52.7%); m.p.,172-173° (after 2-fold recrystallization from ethyl alcohol, 174-175°); a mixture of the yellow prisms with known β-dimethylaminopyridine picrate showed no depression of the melting point.

Found % N 19.77. $C_{13}H_{13}O_7N_5$. Calculated % N 19.95.

Interaction of β-hydroxypyridine chloro-2,4-dinitrophenylate with aniline. a) With heating. 0.30 g of β-hydroxypyridine chloro-2,4-dinitrophenylate [2,4-dinitrophenyl-β-hydroxypyridinium chloride] and 0.19 g of aniline were heated in 10 ml of ethyl alcohol on a boiling-water bath for three hours. After 24 hours, the reddish-brown liquid was filtered from the small amount of dark precipitate, and the filtrate was evaporated under vacuum. The brown crystals were extracted with hot toluene, the solvent was then distilled under vacuum, and the residue was crystallized from ethyl alcohol, 0.06 g (23.1%) of reddish-orange needles of phenyl-2,4-dinitrophenylamine, m.p. 156°, was obtained. A mixture of this material with known phenyl-2,4-dinitrophenylamine melted at the same temperature.

b) At room temperature. 0.25 g of β-hydroxypyridine chloro-2,4-dinitrophenylate and 0.16 g of aniline were mixed with 7 ml of ethyl alcohol and allowed to stand at room temperature for nine months. A small amount of tarry crystals separated from the dark-orange solution. The solvent was evaporated under vacuum, and the residue was extracted with toluene (35 ml). The toluene extract was washed with 3% hydrochloric acid and then with water, and was dried with anhydrous sodium sulfate. After distillation of the toluene under vacuum, the residue was recrystallized from alcohol. The resulting reddish-orange needles, m.p. 156°, weight 0.07 g (32.2%), caused no depression of the melting point when mixed with known phenyl-2,4-dinitrophenylamine.

Interaction of γ-acetamidopyridine chloro-2,4-dinitrophenylate with aniline when heated. A solution of 0.34 g of the chloro-2,4-dinitrophenylate of γ-acetamidopyridine [γ-acetamido-N-2,4-dinitrophenylpyridinium chloride] and 0.18 g of aniline in 10 ml of ethyl alcohol was heated to boiling in a flask fitted with a reflux condenser on a boiling-water bath (three hours). The coarse, heavy, dark-red prisms and fine, reddish-orange needles which separated from the cooled solution stratified on the bottom of the vessel with the prisms on the bottom. The needles, being lighter, became suspended when the solution was agitated, and were filtered separately. The weight was 0.03 g (11.5%) and the m.p. 154°; recrystallized from ethyl alcohol gave 0.015 g of crystals with m.p. 156°. A mixture of these crystals with known phenyl-2,4-dinitrophenylamine melted at the same temperature. The dark-red prisms, 0.20 g, m.p. 218°, were then filtered, and were identified as a molecular compound of γ-acetoamidopyridine chloro-2,4-dinitrophenylate with aniline.

Reaction of γ-phenylaminopyridine chloro-2,4-dinitrophenylate with aniline when heated. 0.37 g of γ-phenylaminopyridine chloro-2,4-dinitrophenylate [2,4-dinitrophenyl-γ-phenylaminopyridinium chloride] and

0.18 g of aniline in 5 ml of ethyl alcohol were heated on a boiling-water bath for five hours. Orange needles separated from the cooled reddish-orange solution after the introduction of a small seed crystal of phenyldinitrophenylamine; weight, 0.06 g (23.1%); m.p., 155°; a mixture of the crystals with known phenyl-2,4-dinitrophenylamine showed no depression of the melting point. Red prisms, identified as a molecular compound of γ-phenylaminopyridine chloro-2,4-dinitrophenylate with aniline, crystallized from the cooled filtrate; weight, 0.19 g; m.p., 210°.

Interaction of β-iodopyridine chloro-2,4-dinitrophenylate with aniline. To a solution of 0.2 g of β-iodopyridine chloro-2,4-dinitrophenylate [N-2,4-dinitrophenyl-β-iodopyridinium chloride] in 8 ml of ethyl alcohol was added 0.09 g of aniline, and the mixture was refluxed on a water bath for three hours. The solution was then evaporated to dryness under vacuum. The residue was washed with hot toluene (7 ml) and crystallized from alcohol. The resulting yellow prisms weighed 0.07 g (77.8%) and melted at 179° after 2-fold recrystallization from alcohol); a mixture of this material with known 2,4-dinitroaniline melted at the same temperature. Phenyl-2,4-dinitrophenylamine was not found in either the toluene extract or the alcohol filtrates.

SUMMARY

1. The reaction of the chloro-2,4-dinitrophenylates of pyridine and its derivatives with aniline was investigated. It was found that this reaction proceeds in different directions depending on the nature of the substituent, its position on the pyridine ring, and the temperature conditions.

2. When electropositive substituents are present on the pyridine ring, the ring N–C bonds in the corresponding chlorodinitrophenylates are stabilized with respect to the action of the base. In this case, rupture of the extra-ring bond occurs, either alone or together with the ring bonds.

3. A shift of the electropositive substituent in the chlorodinitrophenylate of the pyridine base from the β-position to the γ-position increases the stabilizing effect of the substituent on the ring N–C bonds in the reaction with aniline.

4. The investigated conversions of the chloro-2,4-dinitrophenylates of β- and γ-substituted pyridines constitute an example of the general reaction of cleavage of quaternary salts of pyridine, quinoline, and isoquinoline by the action of water, alcohols, aromatic amines, phenols, etc. Rupture of the extra-ring N–C bond proceeds especially easily if the heterocyclic nitrogen atom is bonded to an electronegative radical.

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ON SOME PROPERTIES OF ENOL ACETATES

III. PREPARATION OF FURAN AND PYRAN DERIVATIVES FROM BROMO-SUBSTITUTED ENOL ACETATES

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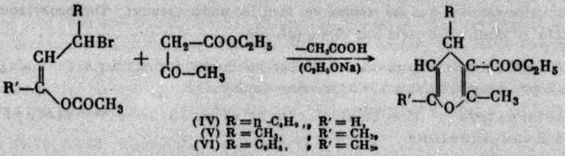
In a preceding communication [1], we described the preparation, in good yield, of 2-methyl-3-carbethoxy-4,5,6,7-tetrahydrocumarone by the condensation of the bromo-substituted enol acetate of cyclohexanone with sodioacetoacetic ester.

In the present work, we synthesized 2-ethoxy-3-carbethoxy-4,5,6,7-tetrahydrocoumarone, in 65% yield, by the condensation of this same bromo-substituted enol acetate with sodiomalonic ester.

Then, by condensing the bromo-substituted enol acetates (I), (II) and (III), having the general formula $R-CHBr-CH=C(OCOCH_3)-R'$,* with sodioacetoacetic ester, we were able to carry out the synthesis of a series of compounds of the pyran group, (IV), (V) and (VI), the formation of which is expressed by the following general scheme:



(IV) $R = n\text{-}C_4H_9$, ; $R' = H$,
(V) $R = CH_3$, ; $R' = CH_3$,
(VI) $R = C_6H_5$, ; $R' = CH_3$.

The bromo-substituted enol acetates (I), (II) and (III) were easily prepared (in yields of from 38 to 57%) by the action of N-bromosuccinimide on the enol acetates of, respectively, enanthole [heptanal], methyl propyl ketone, and benzylacetone. The condensations with sodioacetoacetic ester were carried out under approximately the same conditions that were described in the preceding communication [1]. 2-Methyl-4-butyl-3-carbethoxypyran (IV) was prepared from (I) with a yield of 69%, (II) gave 2,4,6-trimethyl-3-carbethoxypyran (V) in 63.4% yield, and 2,6-dimethyl-4-phenyl-3-carbethoxypyran (VI) was synthesized from (III) with a yield of 61.5%.

Some of the properties of these pyran derivatives were investigated. It was established that when heated with an alcoholic solution of potassium hydroxide, (IV) undergoes hydrolysis with the formation of 2-methyl-4-butyl-3-pyrancarboxylic acid (VII). When (V) and (VI) are treated similarly, along with hydrolysis, decarboxylation occurs, which leads to the formation of 2,4,6-trimethylpyran (VIII) and 2,6-dimethyl-4-phenylpyran (IX), respectively.**

During the interaction of (VII), (VIII) and (IX) with 2,4-dinitrophenylhydrazine sulfate, cleavage of the pyran ring (and in the case of (VII), decarboxylation also) occurred, which resulted in the formation of the bis-2,4-dinitrophenylhydrazones of the corresponding 1,5-dicarbonyl compounds: 3-butyl-5-hexanone-1-al, 4-methyl-2,6-heptanedione, and 4-phenyl-2,6-heptanedione, respectively.

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*The reactions were carried out using compounds in which: (I) $R = n\text{-}C_4H_9$ and $R' = H$; (II) $R = CH_3$ and $R' = CH_3$; (III) $R = C_6H_5$ and $R' = CH_3$.

**Up to the present time, the simplest substituted pyrans have not been prepared [2]. Of the aryl-substituted pyrans, only 2,4,4,6-tetraphenyl-γ-pyran is known [3].

EXPERIMENTAL

1. Preparation of 2-Ethoxy-3-carbethoxy-4,5,6,7-tetrahydrocoumarone

160 ml of anhydrous alcohol was charged to a three-necked flask fitted with a stirrer, a reflux condenser with calcium chloride tube, and a dropping funnel, and 6.9 g of metallic sodium was gradually added. The solution was cooled to room temperature, and, with stirring, 64 g of freshly distilled malonic ester was gradually added followed by 65.7 g of 3-bromo-2-acetoxy-1-cyclohexene.* The reaction mixture was refluxed on a water bath for two hours. The liquid was cooled, suction filtered to remove the precipitated sodium bromide, and the alcohol was distilled under the vacuum of an aspirator (while heated on a water bath). A small amount of water was added to the residue, and the mixture was extracted with ether. The ether extract was dried with sodium sulfate, the ether was distilled, and the residue was distilled under vacuum. After distillation of the unreacted acetoacetic ester, the 2-ethoxy-3-carbethoxy-4,5,6,7-tetrahydrocoumarone was distilled at 120-125° (4 mm). The yield was 46.5 g (65%).

Found %: C 65.23; H 7.23. Saponification number 455.8. $C_{13}H_{18}O_4$. Calculated %: C 65.53; H 7.61. Saponification number 471.

2. Preparation of the Enol Acetate of Benzylacetone

To a solution of 74.1 g of benzylacetone in 153.2 g of acetic anhydride was added 25 drops of concentrated H_2SO_4, and the reaction mixture was allowed to stand at room temperature for 20 days.** The unreacted acetic anhydride was then decomposed by agitation with water, solid sodium carbonate was added to an alkaline reaction, and the reaction product was extracted with ether. The ether extract was washed with a 15% solution of sodium carbonate to complete removal of residual acid, then with water, and dried over sodium sulfate. The ether was distilled under aspirator vacuum, and the residue was distilled under vacuum. The benzylacetone enol acetate distilled at 112-114° (2 mm). The yield was 29.8 g (31.3%).

Found %: C 75.61; H 7.69. Saponification number 309.8; bromine number 81.5. $C_{12}H_{14}O_2$. Calculated %: C 75.76; H 7.42. Saponification number 294.2; bromine number 83.9.

3. Allylic Bromination of the Enol Acetates of Enanthole,*** Methyl Propyl Ketone,**** and Benzylacetone

The bromination was carried out with N-bromosuccinimide by the method described by us for cyclohexanone enol acetate [4]. The yields of bromination products were, respectively, 57, 48.5 and 37.9%.

3-Bromo-1-acetoxy-1-heptane (I) was a colorless liquid with a b.p. of 63-65° (3 mm). The product was not stable toward storage, and it rapidly darkened on standing. This caused inaccuracy in the determination of the bromine content.

Found %: Br 27.12, 27.35. $C_9H_{15}O_2Br$. Calculated %: Br 33.14.

4-Bromo-2-acetoxy-2-pentene (II) was a colorless liquid with a b.p. of 45-47° (3 mm). In contrast to the preceding product, it was stable on storage.

Found %: Br 38.23. $C_7H_{11}O_2Br$. Calculated %: Br 38.59.

1-Bromo-3-acetoxy-1-phenyl-2-butene (III) was a colorless liquid with a b.p. of 122-124° (2 mm).

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*The 3-bromo-2-acetoxy-1-cyclohexane was prepared by bromination of the enol acetate of cyclohexanone with N-bromosuccinimide [4].

**The yield of the enol acetate decreased when the reaction time was less.

***The enanthole acetate was prepared by heating enanthole with acetic anhydride in the presence of sodium acetate [5].

****The methyl propyl ketone enol acetate was prepared by the interaction of methyl propyl ketone with acetic anhydride in the presence of sulfuric acid [6].

Found % Br 28.40. $C_{12}H_{19}O_2Br$. Calculated % Br 29.69.

4. Synthesis of 2-Methyl-4-butyl-3-pyrancarboxylic Acid (VII)

A. Preparation of 2-methyl-4-butyl-3-carbethoxypyran (IV). 40 g of anhydrous alcohol was charged to a three-necked flask fitted with a stirrer, a reflux condenser with calcium chloride tube, and a dropping funnel, and 2.3 g of sodium was gradually added. The solution was then cooled to room temperature, and 26 g of acetoacetic ester was added, with cooling and stirring, followed by 23.5 g of 3-bromo-1-acetoxy-1-heptene. Even in the cold, a precipitate of sodium bromide was formed. The reaction mixture was heated for an hour at a water-bath temperature of 60°. After the liquid was cool, it was suction filtered from the precipitated sodium bromide, and the alcohol was distilled under aspirator vacuum. A small amount of water was added to the residue, and the mixture was extracted with ether. The ether solution was dried with sodium sulfate, and the ether was distilled; the residue was distilled under vacuum. After distillation of the unreacted acetoacetic ester, the ethyl ester of 2-methyl-4-butyl-3-pyrancarboxylic acid was distilled at 118-120° (4 mm); the amount was 15.4 g (69%). The 2-methyl-4-butyl-3-carbethoxypyran was a light-yellow liquid with a distinctive odor.

Found % C 69.62, 69.27; H 9.32, 9.13. Saponification number 259.6. $C_{13}H_{20}O_3$. Calculated % C 69.61; H 8.98. Saponification number 250.1.

B. Hydrolysis of the 2-methyl-4-butyl-3-carbethoxypyran (IV) was carried out by heating it (4.5 g) with 80 ml of an 0.5-N alcoholic solution of potassium hydroxide at the boiling point for two hours. Carbon dioxide was passed into the reaction mixture to remove the excess potassium hydroxide, the liquid was suction filtered from the resulting K_2CO_3 precipitate, and the precipitate was washed with alcohol. The alcohol was distilled from the filtrate under aspirator vacuum. The solid residue (the potassium salt of VII) was dissolved in a small amount of water, the solution was acidified with a 2-N solution of hydrochloric acid, and the resulting acid (VII) was extracted with ether. The ether solution was dried with sodium sulfate, the ether was distilled, and the residue was distilled under vacuum. 2.3 g of (VII) was obtained with a b.p. of 145-147° (4 mm).

Found % C 67.19; H 8.54. Acid number 262.3. $C_{11}H_{16}O_3$. Calculated % C 67.32; H 8.22. Acid number 285.6.

Interaction of acid (VII) with 2,4-dinitrophenylhydrazine. 10 ml of anhydrous alcohol was added to 1 g of 2,4-dinitrophenylhydrazine which had been dissolved, with gentle heating, in 2 ml of concentrated H_2SO_4, and immediately a solution of 0.5 g of (VII) in anhydrous alcohol was added. After some time, a precipitate of 3-butyl-5-cyclohexanone-1-al bis-2,4-dinitrophenylhydrazone formed, and this was separated and recrystallized several times from a mixture of alcohol and ethyl acetate. The red crystals melted at 165° (with decomposition).

Found % N 20.75, 20.82. $C_{22}H_{26}O_8N_8$. Calculated % N 21.08.

5. Synthesis of 2,4,6-Trimethylpyran (VIII)

A. Preparation of 2,4,6-trimethyl-3-carbethoxypyran (V). The following quantities of starting materials were used: 130 ml of anhydrous alcohol, 5.75 g of sodium, 65 g of acetoacetic ester, and 51.7 g of the bromo-substituted enol acetate of methyl propyl ketone. The condensation was carried out under the same conditions used in the preparation of (IV) with the exception that the heating was continued for three hours at reflux temperature. The precipitate of sodium bromide began to form only on heating. Treatment of the reaction mixture and separation and purification of the resulting product was carried out in the manner used in the preceding case. 31 g (63.4%) of 2,4,6-trimethyl-3-carbethoxypyran was obtained in the form of a slightly yellowish liquid with a b.p. of 102-103° (2 mm).

Found % C 67.09; H 7.95. Saponification number 289.1. $C_{11}H_{16}O_3$. Calculated % C 67.32; H 8.22. Saponification number 285.3.

B. Preparation of 2,4,6-trimethylpyran (VIII). 9.8 g of 2,4,6-trimethyl-3-carbethoxypyran was heated to boiling over a period of two hours with 200 ml of an 0.5-N alcoholic solution of potassium hydroxide; during this, the formation of a precipitate of K_2CO_3 was observed on the walls of the flask. Carbon dioxide was passed into the reaction mixture to remove the excess potassium hydroxide, and the resulting K_2CO_3 precipitate was separated and washed with alcohol. The alcohol was distilled from the filtrate, the residue was dissolved in water, and the reaction product was extracted with ether. The extract was dried with sodium sulfate, the ether was distilled, and the residue was distilled under vacuum.

3.82 g (61.5%) of 2,4,6-trimethylpyran was obtained. It was a colorless liquid with a characteristic odor and a b.p. of 70-72° (2 mm).

Found %: C 77.12, 76.98; H 9.65, 9.42. $C_9H_{12}O$. Calculated %: C 77.37; H 9.74.

The interaction of (VIII) with 2,4-dinitrophenylhydrazine under the conditions described in the preceding experiment gave 4-methyl-2,6-heptanedione bis-2,4-dinitrophenylhydrazone – red crystals with an m.p. of 116° (with decomposition) (from a mixture of alcohol and ethyl acetate).

Found %: N 21.86. $C_{20}H_{22}O_8N_8$. Calculated %: N 22.23.

6. Synthesis of 2,6-Dimethyl-4-phenylpyran (IX)

A. Preparation of 2,6-dimethyl-4-phenyl-3-carbethoxypyran (VI). The following amounts of starting materials were used: 65 ml of anhydrous alcohol, 2.3 g of sodium, 26 g of acetoacetic ester, and 26.9 g of the bromo-substituted enol acetate of benzylacetone. The condensation and treatment of the reaction mixture were carried out as described for the preceding experiment. 13.5 g (52.2%) of 2,6-dimethyl-4-phenyl-3-carbethoxypyran was obtained in the form of a yellowish liquid with a b.p. of 148-151° (2 mm).

Found %: C 74.14; H 6.90. Saponification number 202.5. $C_{16}H_{18}O_3$. Calculated %: C 74.39; H 7.02. Saponification number 216.3.

B. Preparation of 2,6-dimethyl-4-phenylpyran (IX). 12.9 g of (VI) and 200 ml of an 0.5-N alcoholic solution of potassium hydroxide were used. The reaction and treatment of the product were carried out as in the preceding experiment. 5.2 g (55.6%) of 2,6-dimethyl-4-phenylpyran was obtained. It was a light-yellow liquid with a b.p. of 135-136° (3 mm).

Found %: C 83.62; H 7.71. $C_{13}H_{14}O$. Calculated %: C 83.83; H 7.57.

Interaction of (IX) with 2,4-dinitrophenylhydrazine gave 4-phenyl-2,6-heptanedione 2,4-dinitrophenylhydrazone. The brown crystals melted at 138° (with decomposition) (from a mixture of alcohol and ethyl acetate).

Found %: N 19.63. $C_{25}H_{24}O_8N_8$. Calculated %: N 19.86.

SUMMARY

1. The condensation of 3-bromo-2-acetoxy-1-cyclohexene with sodiomalonic ester gave 2-ethoxy-3-carbethoxy-4,5,6,7-tetrahydrocoumarone; this product has not previously been described in the literature.

2. It was shown that condensation of brominated enol acetates of the type $R-CHBr-CH=C(OCOCH_3)R'$ with sodioacetoacetic ester leads to the formation of the corresponding pyran derivatives. The following compounds were obtained: 2-methyl-4-butyl-3-carbethoxypyran, 2,4,6-trimethyl-3-carbethoxypyran, and 2,6-dimethyl-4-phenyl-3-carbethoxypyran.

3. It was established that when heated with alcoholic alkali, 2-methyl-4-butyl-3-carbethoxypyran is converted to 2-methyl-4-butyl-3-pyrancarboxylic acid. When heated with alcoholic alkali under the same conditions, 2,4,6-trimethyl-3-carbethoxypyran and 2,6-dimethyl-4-phenyl-3-carbethoxypyran undergo hydrolysis and also decarboxylation with the formation of 2,4,6-trimethylpyran and 2,6-dimethyl-4-phenylpyran, respectively. None of these substituted pyrans have been described in the literature.

4. The bromo-substituted enol acetates of enanthole, methyl propyl ketone, and benzylacetone were prepared for the first time by bromination of the corresponding aldehyde (enanthole) and methyl ketones (methyl propyl ketone and benzylacetone) with N-bromosuccinimide.

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ON THE SYNTHESIS AND STRUCTURE OF THE o-SULFOBENZOYL DICHLORIDES

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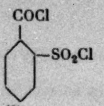
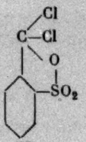
The o-sulfobenzoyl dichlorides have found widespread application in organic synthesis, particularly in the synthesis of sulfophthalein indicators [1-6].

The o-sulfobenzoyl dichlorides have been isolated in two isomeric forms – the symmetrical and lactone structures [7-9].



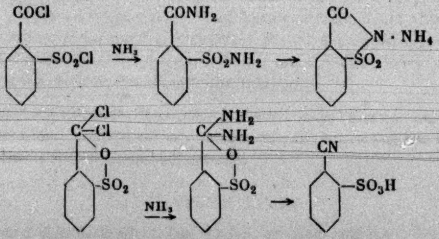
(I)



(II)

One of the dichlorides has an m.p. of 40°, decomposes under the action of ammonia [7, 10], and withstands heating under vacuum to 183° [11]. The second has an m.p. of 79°, is stable to the action of ammonia at a temperature of about 20°, and decomposes during vacuum distillation at 20-30 mm [7] and at 15 mm [11] to o-chlorobenzoyl chloride and sulfur dioxide. An attempt to convert one isomer into the other failed [7]. The two dichlorides form an eutectic mixture which melts at 21° [13] or 21.5° [8].

The literature contains more than one opinion on the question of which dichloride has the symmetrical and which the lactone structure. According to the data of certain investigators [7, 8], isomer (I) has the m.p. of 79°, while (II) has the 40° m.p.. The authors came to this conclusion on the basis of the reactions occurring during the action of ammonia on (I) and (II).



However, in more recent investigations [9], it was shown that the action of ammonia on symmetrical dichlorides can also lead to the formation of CN-groups, provided that the chlorocarbonyl groups are ortho to each other. By comparing the absorption spectra of o-sulfobenzoic acid and its dichlorides with the spectra of o-toluenesulfonic acid and its chloride, these same investigators came to the conclusion that the dichloride with an m.p. of 40° has the symmetrical structure, while the one with the m.p. of 79° has the lactone structure.

According to information in the literature, an eutectic mixture of isomeric dichlorides is obtained by the action of phosphorus pentachloride on the potassium acid salt [7, 12], the dipotassium salt [11, 13], and the ammonium acid salt [6, 11] of o-sulfobenzoic acid.

The interaction of dipotassium o-sulfobenzoate with phosphoryl chloride at 130° (under pressure) leads to the dichloride with an m.p. of 40° [7].

The dichloride with an m.p. of 79° has not been obtained by direct synthesis; it can be isolated from the mixture of isomers after decomposition with ammonia of the dichloride with an m.p. of 40° [7, 10]. The use of thionyl chloride leads not to the dichloride, but to the anhydride of o-sulfobenzoic acid [14, 15].

The aim of the present investigation was the development of a convenient method for the preparation of the o-sulfobenzoyl dichlorides in the form of a mixture of the two isomers.

The interaction of phosphorus pentachloride with the alkali metal salts of o-sulfobenzoic acid can be carried out by heating the reagents on a water bath [11] or by triturating them in a mortar [7]. The latter method has only preparative significance.

Heating a mixture of the dipotassium salt of o-sulfobenzoic acid and phosphorus pentachloride on a steam bath did not give positive results, even at 120-130°.

Carrying out the reaction in the presence of phosphoryl chloride by adding the dipotassium sulfobenzoate to a mixture of phosphorus pentachloride and a small amount of phosphoryl chloride was found to be very effective. The reaction proceeded very vigorously with the liberation of heat. Adding the dipotassium salt and the phosphorus pentachloride portion-wise and separately, maintained the reaction mass as a liquid and made continuous stirring possible over the entire course of the synthesis.

As recommended by some investigators [7], the reaction mixture was washed several times with ice water to remove the potassium chloride formed during the reaction (decomposition of the phosphoryl chloride occurred simultaneously). However, after being washed with water, the dichlorides became unstable at room temperature, apparently owing to insignificant amounts of residual water. During drying, even with such mild drying agents as sodium sulfate, evolution of heat by the oil and evolution of hydrogen chloride and sulfur dioxide were observed. Therefore, this method of treating the reaction mixture had to be abandoned.

Almost quantitative separation of the potassium chloride was accomplished by extraction of the dichlorides from the reaction mass with benzene or chloroform. The solution of dichlorides was then distilled at 15-20 mm absolute pressure. Contrary to statements in the literature [7, 11], there was practically no decomposition of the dichloride with an m.p. of 79° during the distillation, and we repeatedly separated it from the eutectic mixture of the two isomers.

The isomeric dichlorides obtained by the above method did not contain chlorine in the ring, showing the absence of o-chlorobenzoyl chloride which is formed in the case of the decomposition of the isomer with an m.p. of 79°. Hydrolysis of the dichlorides with water gave a quantitative yield of pure o-sulfobenzoic acid, in which there was no chloride, which also indicated that there was no o-chlorobenzoyl chloride in the dichloride mixture.

These experimental data indicate that the dichloride with an m.p. of 79° is thermally stable during distillation at 15-20 mm (b.p. 165-176°).

With equimolar amounts of dipotassium o-sulfobenzoate and phosphorus pentachloride, the yield of dichlorides varied in the range of 50-60%; it increased to 74-75% when the amount of phosphorus pentachloride was increased to 15% excess with respect to the theoretical amount.

In view of the uncertainty and contradictions in the information concerning which of the o-sulfobenzoyl dichlorides should be assigned the symmetrical and which the lactone structure, it was of interest to compare the half-wave potentials ($E_{1/2}$) of these dichlorides with those of the dichlorides of o-phthalic acid. The latter also forms two dichlorides having symmetrical and lactone structures; the structure and physical constants for each of them have been established [16].

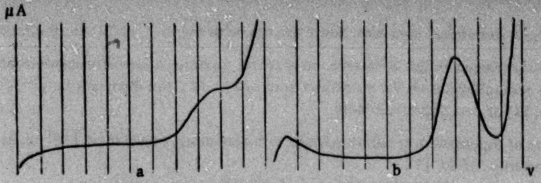


Fig. 1. o-Sulfobenzoyl dichloride with an m.p. of 40°: a) ordinary wave (S = 1/15); b) derivative wave (S = 1/1).

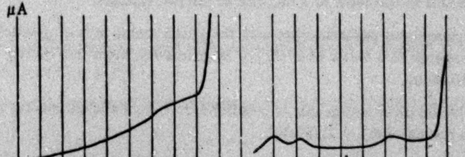


Fig. 2. o-Sulfobenzoyl dichloride with an m.p. of 79°: a) ordinary wave (S = 1/30); b) derivative wave (S = 1/1).

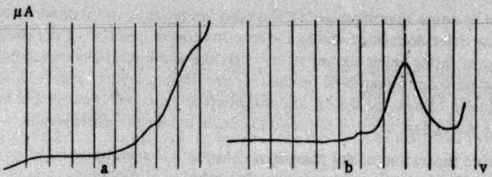


Fig. 3. o-Phthaloyl dichloride (symmetrical structure): a) ordinary wave (S = 1/15); b) derivative wave (S = 1/5).

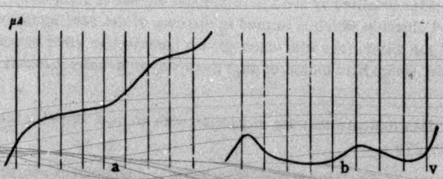
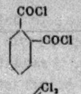
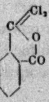


Fig. 4. o-Phthaloyl dichloride (lactone structure): a) ordinary wave (S = 1/5); b) derivative wave (S = 1/5).

The individual dichlorides of o-sulfobenzoic acid and o-phthalic acid were synthesized in the pure form by methods described in the literature [7, 10, 16].

The results of the polarographic measurements are presented in the Table and in Figs. 1-4.

Half-Wave Potentials of the Dichlorides of o-Sulfobenzoic and o-Phthalic Acids (with respect to a saturated calomel electrode)

Dichloride	Melting point	Structural formula	$E_{1/2}$ of the polarographic wave (v)	
			ordinary	derivative*
o-Sulfobenzoyl dichloride	40°	—	−1.56	−1.60
o-Sulfobenzoyl dichloride	79	—	−1.20	−1.26
Symmetrical o-phthaloyl dichloride	16		−1.58	−1.60
o-Phthaloyl dichloride with lactone structure	80		−1.20	−1.22

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*Recording of the derivative waves was necessary owing to the lack of clarity in the ordinary waves of the o-sulfobenzoyl dichloride, with an m.p. of 79°, and of the o-phthaloyl dichloride, with an m.p. of 16°.

It may be seen from the Table and the figures that the values of the half-wave potentials are in good agreement: 1) for symmetrical o-phthaloyl dichloride and the o-sulfobenzoyl dichloride with an m.p. of 40° and 2) for the o-phthaloyl dichloride with a lactone structure and the o-sulfobenzoyl dichloride with an m.p. of 79°.

These numerical values of $E_{1/2}$ permit the conclusion that the o-sulfobenzoyl dichloride with an m.p. of 40° has the symmetrical structure, while the one with an m.p. of 79° has the lactone structure.

These results confirm the data of Scheiber and Knothe [9].

EXPERIMENTAL

Synthesis of the mixture of isomeric dichlorides. Into a three-necked flask fitted with a stirrer and a reflux condenser, the end of which was connected to a calcium chloride tube, was introduced 51 g of phosphoryl chloride, and 70 g of carefully ground phosphorus pentachloride was added with stirring. 15 g of dipotassium o-sulfobenzoate was then added; the mixture rapidly liquefied, and another 74 g of phosphorus pentachloride was then added. Exothermic heat raised the temperature to 45-50°. 68.5 g of the dipotassium salt was added portion-wise over a period of an hour at a temperature of 80-90°. The mixture was heated to boiling (115-117°) and stirred for three hours; it was then cooled to 50°, 75 ml of benzene or chloroform was added, the mixture was stirred for 5-10 minutes, and cooled to 20°. The potassium chloride was filtered. A large part of the benzene and phosphoryl chloride was first distilled at atmospheric pressure, and the remainder of the benzene and phosphoryl chloride was distilled at 20-25 mm; the dichlorides came over at 165-170°. The yield was 52-54 g (72.5-75.3%).

Found %: Cl (in side chain) 29.5-29.8; Cl (total) 29.5-29.8. $C_7H_4O_3SCl_2$. Calculated %: Cl (in side chain) 29.66.

The Cl in the side chain was determined after hydrolysis of the dichloride with a 1.0-N solution of NaOH; Cl in the ring was determined by the Stepanov method, but ethyl alcohol was substituted for butyl.

The mixture of isomeric dichlorides was a colorless, oily liquid, from which a large quantity of crystals separated on standing. Hydrolysis of the dichlorides with water gave a quantitative yield of o-sulfobenzoic acid with an m.p. of 67-68° (literature value, 68-69° [17], 70° [18]).

Preparation of the dichloride with an m.p. of 79°. The distilled mixture of isomeric dichlorides (20 g) was dissolved in 20 ml of chloroform. The solution was cooled to 3-5°, and, over a period of 15 minutes, a 25% solution of ammonia was added to a weakly alkaline reaction (phenolphthalein). The excess ammonia was neutralized with hydrochloric acid (congo indicator). The chloroform layer was separated, dried with sodium sulfate, and treated with activated carbon. The chloroform was distilled at 80-100 mm. The residue crystallized in the flask. The yield was 2 g. M.p. 72.7-73.5° (literature value, 75.9° [8], 79° [7]). After several washings with petroleum ether, the m.p. was 77-78°.

Preparation of the dichloride with an m.p. of 40°. The distilled mixture of isomeric dichlorides (20 g) was allowed to stand for several days at a temperature of about 20°. The precipitated crystals were filtered and washed with petroleum ether. M.p. 38.0-39.0°.

Measurement of the half-wave potentials ($E_{1/2}$). Measurement of the half-wave potentials was carried out with a Heyrovsky-type micropolarograph with a dropping mercury electrode having forced interruption of the drops (with a period of 0.4 seconds). A saturated calomel electrode served as the anode. The solutions investigated polarographically were 0.001 M with respect to the dichloride and 0.25 M with respect to lithium chloride; the solvent was 50% alcohol. The maxima were suppressed with methyl red. The air was purged from the solutions by passing hydrogen through them for 15 minutes prior to recording the curve. The derivative curves were taken with a Vogel and Riha circuit incorporated into the polarograph circuit.

SUMMARY

1. A method satisfactory for technical use was developed for the preparation of the mixture of isomeric o-sulfobenzoyl dichlorides in yields of 72-75% of theoretical.

2. The reports in the literature that the dichloride with an m.p. of 79° is thermally unstable when distilled at a pressure of 15 mm were not confirmed. Distillation gave a mixture of the isomeric dichlorides.

3. A comparison of the half-wave potentials of the o-sulfobenzoyl dichlorides with those of the o-phthaloyl dichlorides permitted the conclusion that the o-sulfobenzoyl dichloride with an m.p. of 40° has the symmetrical structure, and the one with an m.p. of 79° has the lactone structure.

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THE PREPARATION OF Δ^{23}-3-KETO-24,24-DIPHENYLCHOLENE

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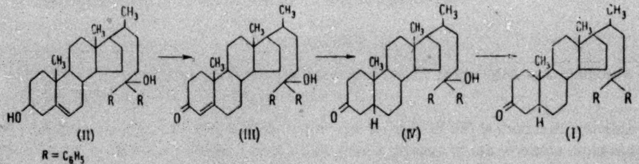
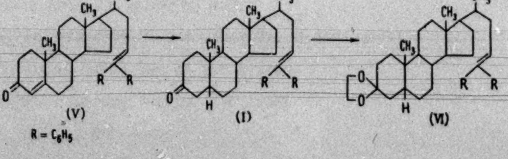
Δ^{23}-3-Keto-24,24-diphenylcholene (I) is of interest as a starting material for the synthesis of pregnane-3,20-dione from Δ^{5}-3β-hydroxycholenic acid. It was prepared from Δ^{5}-3β,24-dihydroxy-24,24-diphenylcholene (II) according to the scheme



Δ^{5}-3β,24-Dihydroxy-24,24-diphenylcholene (II) was subjected to Oppenauer oxidation [1, 2] with cyclohexanone in the presence of aluminum isopropoxide. The substance, m.p. 136-137°, separated from the reaction mixture by appropriate treatment and recrystallization from methyl alcohol was, on the basis of the analytical data, an adduct of Δ^{4}-3-keto-24-hydroxy-24,24-diphenylcholene (III) with 0.5 molecule of methyl alcohol. The reduction of (III) was carried out in pyridine solution at room temperature and in the presence of palladium on calcium carbonate (2% Pd), since it is well known that the use of palladium on carbon or other carriers for the hydrogenation of Δ^{4}-3-ketosteroids leads to the formation of saturated 3-ketones of the normal series [3, 4]. From this reaction, we obtained a ketone with an m.p. of 181.5-182.5°, namely, 3-keto-24,hydroxy-24,24-diphenylcholane (IV); this ketone has not been described in the literature. Dehydration of this ketone by refluxing in glacial acetic acid [5] gave a previously unknown ketone (I) with an m.p. of 150-152°.

We were also able to prepare ketone (I) by a simpler method from $\Delta^{4,23}$-3-keto-24,24-diphenylcholadiene (V) by catalytic hydrogenation.



During reduction of the substance (V) with palladium on calcium carbonate (2% Pd), 1 mole of hydrogen was absorbed, and a 91% yield of a substance with an m.p. of 150.5-152° was obtained; this was identified as our previously prepared (I).

Thus, under the hydrogenation conditions used, only one of the double bonds in (V), in the 4,5-position, was saturated. By refluxing, in an apparatus with a Dean and Stark head, a benzene solution of ketone (I) with excess ethylene glycol in the presence of a small amount of p-toluenesulfonic acid we obtained Δ^{23}-3-keto-24,24-diphenylcholene-3-ethylene ketal (VI) with an m.p. of 140.5-141.5°.

A study of conditions for the conversion of (VI) to ketone (I) showed that the best results are obtained when the ketal is refluxed for a considerable length of time in acetone solution with the addition of p-toluenesulfonic acid [6]; the reaction does not go to completion when (VI) is refluxed in aqueous acetic acid.

EXPERIMENTAL

Preparation of Δ^4-3-keto-24-hydroxy-24,24-diphenylcholene (III) containing 0.5 molecule of methyl alcohol. 3 g of Δ^5-3β,24-dihydroxy-24,24-diphenylcholene (II; m.p. 168-170°) and 85 ml of toluene were placed in a flask fitted with a thermometer, a stirrer, and a straight condenser. The mixture was heated to boiling, 15 ml of toluene was distilled, and then 2.4 ml of a 37% solution of aluminum isopropoxide in toluene was rapidly added, followed by another 8 ml of toluene. 10 ml of toluene was distilled, 14.32 g of cyclohexanone in 15 ml of toluene was added, and the reaction mixture was heated for 27 minutes; the heating was controlled so that the toluene distilled slowly. The reaction mixture was cooled, and a solution of 5.16 g of Seignette's salt [potassium sodium tartrate] in 5.5 ml of water was added. The aqueous layer was separated and extracted with toluene. The toluene solutions were combined and concentrated under vacuum at 35-40°, and the residual toluene was distilled at 40-60° and 1 mm. A yellow, oily substance remained, which crystallized when triturated with methyl alcohol. Recrystallization from methyl alcohol gave 2.17 g (70.4%) of a substance with an m.p. of 134-135.5°. A second recrystallization and drying of the crystals under vacuum at 70° increased the m.p. to 136-137°; $[\alpha]_D^{20}$ +59.2° (2% in chloroform). The substance was readily soluble in acetone, chloroform, and benzene, and difficultly soluble in alcohol.

Found %: C 83.21; H 8.92. $C_{36}H_{46}O_2 \cdot {}^1\!/_2CH_4O$. Calculated %: C 83.22; H 9.18.

Preparation of 3-keto-24-hydroxy-24,24-diphenylcholane (IV). The reduction of Δ^4-3-keto-24-hydroxy-24,24-diphenylcholene (2.7 g) was carried out in 12 ml of pyridine in the presence of 1.68 g of palladium on calcium carbonate (2.08% Pd). Over a period of three hours, 1 mole of hydrogen was absorbed, and the hydrogenation was then discontinued. The pyridine solution was poured into cold water and neutralized with hydrochloric acid; the hydrogenation product was extracted with chloroform. The chloroform solution was washed with dilute solutions of hydrochloric acid and sodium bicarbonate and then with water. The chloroform was distilled under vacuum, and the residue was washed with methyl alcohol. 2.54 g (96.6%) of a substance with an m.p. of 180-181.5° was obtained. Recrystallization from acetone and drying of the crystals at 100° under vacuum increased the m.p. to 181.5-182.5°; $[\alpha]_D^{20}$ +26.9° (2% in chloroform). The substance was readily soluble in benzene and chloroform and sparingly soluble in alcohol and ether.

Found %: C 84.35; H 9.15. $C_{36}H_{48}O_2$. Calculated %: C 84.32; H 9.43.

Preparation of Δ^{23}-3-keto-24,24-diphenylcholene (I) from 3-keto-24,24-diphenylcholane (IV). 0.5 g of (IV) was refluxed for 3.5 hours with 4 ml of glacial acetic acid. On cooling of the reaction mixture, a crystalline precipitate formed; this was filtered, washed with methyl alcohol, and dried. 0.43 g (89.2%) of a substance with an m.p. of 149.5-151° was obtained. Recrystallization of the crystals from a mixture of alcohol and acetone increased the m.p. to 150-152°; $[\alpha]_D^{20}$ +55.8° (2% in chloroform). The substance was readily soluble in ether, chloroform and benzene, soluble in acetone, and sparingly soluble in alcohol.

Found %: C 87.47; H 9.28. $C_{36}H_{46}O$. Calculated %: C 87.39; H 9.37.

Preparation of Δ^{23}-3-keto-24,24-diphenylcholene (I) from $\Delta^{4,23}$-3-keto-24,24-diphenylcholadiene (V). 10 g of $\Delta^{4,23}$-3-keto-24,24-diphenylcholadiene (m.p. 138-139°) in 50 ml of dry pyridine was reduced in the presence of 6 g of palladium on calcium carbonate (2.08% Pd). The absorption of hydrogen (1 mole) ceased after 8.5 hours. The catalyst was filtered and washed with a small amount of pyridine; the pyridine solution was poured, with stirring, into cold water, and a dilute solution of hydrochloric acid was added until the solution was acid, as shown by congo indicator. The substance separated first in the form of an oil, which rapidly crystallized; it wss extracted with ether. The ether extract was washed with dilute solutions of hydrochloric acid and sodium bicarbonate and then with water. It was dried with sodium sulfate. The ether was distilled under vacuum, and the residue was recrystallized from a mixture of 250 ml of alcohol and 100 ml of acetone. 8.26 g of a substance with an m.p. of 150.5-152° was obtained. An additional 0.88 g of the substance, m.p. 150-152°, was isolated from the filtrate. The total yield was 9.14 g (91%). A mixture of this material with a sample of the Δ^{23}-3-keto-24,24-diphenylcholene (I) prepared previously, showed no depression of the melting point.

Preparation of Δ^{23}-3-keto-24,24-diphenylcholene-3-ethylene ketal (VI). 12 g of Δ^{23}-3-keto-24,24-diphenylcholene, 12 ml of ethylene glycol, 360 ml of benzene, and 0.5 g of p-toluenesulfonic acid were refluxed for eight hours in an apparatus with a Dean and Stark head; water was separated during the reaction. The reaction mixture was cooled, a solution of potassium hydroxide in methyl alcohol was added, and the mixture was agitated with water. Ether was added, since separation of the layers was poor. The ether-benzene layer was washed three times with water, dried with anhydrous sodium sulfate, and the solvents were distilled under vacuum. The residue was recrystallized from 300 ml of acetone. 12.14 g (92.8%) of the ketal was obtained; m.p. 140.5-141.5°, $[\alpha]_D^{20}$ +52.2° (2% in chloroform). An additional 0.3 g of the substance, m.p. 139-140.5°, was isolated from the filtrate. The total yield was 12.44 g (95.1%). The substance was soluble in chloroform, benzene, and ether and sparingly soluble in alcohol and acetone.

Found %: C 84.67; H 9.37. $C_{38}H_{50}O_2$. Calculated %: C 84.71; H 9.35.

Conversion of ketal (VI) to ketone (I). a) 2 g of ketal (VI) was dissolved in 100 ml of dry acetone; 0.1 g of p-toluenesulfonic acid was added, and the mixture was refluxed for 14 hours. The solution was concentrated under vacuum to half its volume, 50 ml of water was added, and the resulting precipitate was filtered, washed with water to a neutral reaction, and dried under vacuum at 60°. Recrystallization from 60 ml of a mixture of alcohol and acetone (2.5 : 1) gave 1.55 g (84.4%) of a substance with an m.p. of 149-150°. A second recrystallization increased the m.p. to 150-152°. The first filtrate was evaporated to dryness under vacuum. The residue was again treated with acetone in pyridine in the presence of p-toluenesulfonic acid, as described above. An additional 0.11 g of the material, m.p. 149-150°, was obtained. The total yield was 1.66 g (90.4%).

b) 0.3 g of ketal (VI), 6 ml of glacial acetic acid, and 2 ml of water were refluxed for 25 minutes with stirring. 4 ml of glacial acetic acid was added, and refluxing was continued for another 25 minutes. The mixture was cooled, and the precipitate was filtered, washed with water to a neutral reaction, and dried. 0.27 g of a substance with an m.p. of 120-145° was obtained.

SUMMARY

Δ^{23}-3-Keto-24,24-diphenylcholene, which has not previously been described in the literature, was prepared by two methods: from Δ^{5}-3β,24-dihydroxy-24,24-diphenylcholene and from $\Delta^{4,23}$-3-keto-24,24-diphenylcholadiene.

Δ^{23}-3-Keto-24,24-diphenylcholene-3-ethylene ketal was also prepared. Conditions for its conversion to the 3-ketone were determined.

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THE PREPARATION OF PREGNANE-3,20-DIONE FROM Δ^{23}-3-KETO-24,24-DIPHENYLCHOLENE-3-ETHYLENE KETAL

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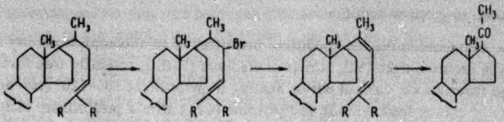
In the course of work on the synthesis of pregnane-3,20-dione, we investigated the bromination with N-bromosuccinimide of Δ^{23}-3-keto-24,24-diphenylcholene-3-ethylene ketal [1] and the dehydrobromination of the resulting 22-bromide.

In 1942, Ziegler and co-workers [2] showed that during the action of N-bromosuccinimide on unsaturated compounds, bromination occurs alpha to the double bond. Later, this reaction found widespread application, and, in particular, has been used in the chemistry of steroids for the conversion of compounds containing the Δ^{23}-24,24-diphenylcholene group (I) through the 22-bromide (II) and $\Delta^{20,23}$-choladiene (III) to the corresponding 20-ketosteroids (IV) according to the scheme:



(I) (II) (III) (IV)

$R = C_6H_5$

The literature has repeatedly contained reports of the synthesis of various 20-ketosteroids from Δ^{5}-3β-hydroxycholenic acid [3, 4], 3β-hydroxyallocholanic acid [5], lithocholic acid [5], and desoxycholic acid [6, 7] by methods in which the last stages were carried out by the above scheme. However, the yields of (III) obtained from (I) for various compounds of this series, and sometimes for the same compound, varied considerably. For example, according to the data of Meystre and co-workers [6], the conversion of Δ^{23}-3α,12α-diacetoxy-24,24-diphenylcholene to $\Delta^{20,23}$-choladiene proceeds with a yield of 82%, while Casanova, Shoppee and Summers [7] indicated that considerable difficulty is encountered in carrying out this reaction. The authors reported that after discussing the reaction conditions with Wettstein, they were able to obtain what they considered satisfactory yields of choladiene (23.7-40.6%* in five experiments and 75% in one experiment under the same conditions). In connection with this, a study of the conversions (I) → (II) and (II) → (III) appeared to be of definite interest.

The present communication presents the results obtained during the bromination with N-bromosuccinimide of Δ^{23}-3-keto-24,24-diphenylcholene-3-ethylene ketal (V) and the subsequent conversion of the bromide (VI) to the previously undescribed $\Delta^{20,23}$-3-keto-24,24-diphenylcholadiene-3-ethylene ketal (VII) and $\Delta^{20,23}$-3-keto-24,24-diphenylcholadiene (VIII). The latter was oxidized with chromium trioxide to pregnane-3,20-dione.

The work was begun with a study of the dehydrobromination reaction. For this purpose, ketal (V) was brominated by the method common for analogous compounds — by refluxing in carbon tetrachloride with N-bromosuccinimide under illumination. After separation of the succinimide, the resulting bromide, without isolation, was further converted to choladiene. According to the literature, elimination of hydrogen bromide from C_{22}

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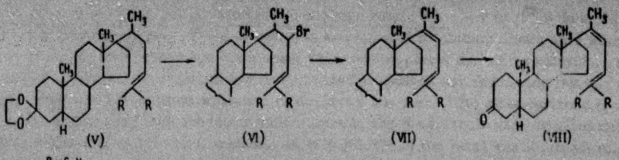
*The amount of material isolated from the filtrates in these experiments was not reported.



(V) (VI) (VII) (VIII)

$R = C_6H_5$

bromides is accomplished by refluxing in carbon tetrachloride [3, 6, 7], in a mixture of carbon tetrachloride and glacial acetic acid [5], and in dimethylaniline [3, 4, 5] and also by heating with pyridine [8].

According to our observations, when dehydrobromination of (VI) is carried out in dimethylaniline (by refluxing for ten minutes), considerable tarring of the reaction products occurs. Therefore, this method was abandoned. When a solution of (VI) in carbon tetrachloride was refluxed (6.5 hours), the resulting compound contained 6% bromine (which corresponds to 46% of the monobromide of the ketal). A more detailed study of the hydrobromination reaction showed that the elimination of hydrogen bromide has already begun during the bromination process (four minutes after the beginning of the reaction). During the subsequent refluxing of the reaction mixture in carbon tetrachloride, the rate of the dehydrobromination reaction gradually decreases, and the process has practically stopped after 10-12 hours, although at this time only about 69% of the theoretical amount of hydrogen bromide has been evolved. It is possible that the equilibrium (VI) ⇌ (VII) is established during the process.

Since the hydrogen bromide evolved during the bromination leads to partial saponification of the ketal group (determined by spectroscopic analysis), which can cause side bromination reactions in the α-position to the 3-keto group, we carried out an experiment in which a small amount of pyridine was added to the reaction mixture. In this case also, after dehydrobromination in carbon tetrachloride, a substance containing 6.1% bromine was obtained. These results indicate that dehydrobromination in carbon tetrachloride at reflux temperature fails, by a considerable extent, to go to completion.

A change in the dehydrobromination conditions permitted us to accomplish readily the almost complete elimination of hydrogen bromide from (VI). Crude choladiene (VII), practically free from brominated impurities, was obtained when the reaction was carried out by heating in pyridine at 105-110° (two hours), by refluxing for two hours in a mixture of carbon tetrachloride and pyridine (4 : 1) after a preliminary refluxing in carbon tetrachloride (five hours), and by refluxing in glacial acetic acid (20 minutes). Interesting results were obtained during an attempt to carry out the dehydrobromination of (VI) in pyridine at room temperature. Under these conditions, along with choladiene, a substance which was readily soluble in alcohol was obtained. It contained nitrogen and bromine, and in aqueous-alcoholic solution it gave a precipitate with silver nitrate. On the basis of the analytical data and the ease of solution in alcohol and hot water, it may be assumed that this compound is the pyridine salt of the monobromide of 3-keto-24,24-diphenylcholene-3-ethylene ketal. Evolution of hydrogen bromide was not detected when this pyridine salt was heated (refluxed four hours) in carbon tetrachloride.

TABLE 1

Expt. No.	Amount of CCl_4 used	Excess of N-bromosuccinimide (%)	Bromination time (in min)	Yield of (VII) (in %)	Melting point of (VII)	Yield of pure (VII) with m.p. of 193.5-196.5° (in %)
1	20	6—7	5.5	51.2	189—193.5°	44.4
2	20	6—7	9—10	53.2	189—193.5	46.2
3 *	20	6—7	9—10	49.7	188—192.5	—
4	20	6—7	20	53.2	189—193.5	46.2
5	20	15	9—10	58.2	189.5—193.5	50.5
6	45	15	9—10	65.3	190—193	56.7
7	45	20	9—10	63.25	191—193	55.2
8	80	15	9—10	72.3	191—192.5	65

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* Experiment 3 was carried out without the addition of pyridine during bromination. The resulting reaction product was subjected, before purification, to the action of ethylene glycol in the presence of p-toluenesulfonic acid.

The investigation of the bromination of ketal (V) was carried out without isolating the bromide (V), which was subjected to dehydrobromination by refluxing in a mixture of carbon tetrachloride and pyridine (4 : 1), i.e., under conditions providing for complete elimination of the hydrogen bromide. A small amount of pyridine was added to the reaction mixture during bromination in order to prevent saponification of the ketal group. We determined the effect of the following variables on the yield of choladiene (VII): bromination time, excess of N-bromosuccinimide, and amount of carbon tetrachloride. The results of the experiments are presented in Table 1 (in all experiments, 1 g of ketal was used).

The data obtained show that a change in the bromination time from 5.5 to 20 minutes has almost no effect on the yield of (VII) (Experiments 1, 2 and 4); an increase in the excess amount of N-bromosuccinimide to 15% leads to an increase in the yield (Experiments 2 and 5). The yield of (VII) increased considerably with an increase in the amount of carbon tetrachloride present during bromination (Experiments 5 and 8).

The conversion of ketal (VII) to ketone (VIII) was carried out by refluxing (14 hours) an acetone solution of (VII) in the presence of p-toluenesulfonic acid. Oxidation of ketone (VIII) with chromium trioxide gave pregnane-3,20-dione.

EXPERIMENTAL

Investigation of the Dehydrobromination Reaction During the Preparation of $\Delta^{20,23}$-3-Keto-24,24-diphenylcholadiene-3-ethylene Ketal (VII)

a) Dehydrobromination in carbon tetrachloride and the kinetics of the reaction. 1 g of Δ^{23}-3-keto-24,24-diphenylcholene-3-ethylene ketal (V), m.p. 140.5-141.5°, was dissolved in 20 ml of dry carbon tetrachloride, 0.332 g of 99.5% N-bromosuccinimide was added, and the mixture was refluxed for twelve minutes in a stream of nitrogen and under illumination by a lamp (500 W) with a reflector. The evolution of hydrogen bromide began four minutes after the reaction was started; the hydrogen bromide was absorbed in an 0.1-N solution of sodium hydroxide. At the conclusion of the bromination, the excess alkali was back-titrated. 1.7 ml of the 0.1-N NaOH had been tied up. The reaction mixture was cooled with ice, the precipitated succinimide was filtered, and the filtrate was boiled for twelve hours in a flask fitted with a dropping funnel, a condenser arranged for distillation, and a receiver, which was connected to a scrubber containing an 0.1-N solution of sodium hydroxide. As the carbon tetrachloride distilled, a corresponding amount of fresh solvent was added. At specific time intervals, the distillate was collected and washed several times with water, and the solution of alkali was replaced. The aqueous extracts were combined with the alkaline solution, and the excess alkali was back-titrated. The results are presented in Table 2.

TABLE 2

Dehydrobromination time (in hrs)	Amount of 0.1-N NaOH reacted with HBr (in ml)		Amount of HBr evolved (in %)
1	3	for each hour	16.2
2	2.72		30.8
3	2.4		43.7
6	2.25	for each 3 hours	55.9
9	0.59		59
12	0.23		60.3

A total of 12.89 ml of the 0.1-N solution of sodium hydroxide was reacted during the bromination and hydrobromination; this corresponds to 69.4% of the theoretical amount of hydrogen bromide. At the conclusion of the reaction, the solvent was distilled under vacuum. The tarry residue was ground with alcohol, filtered, and washed with alcohol. 0.85 g of a substance with an m.p. of 157-171° was obtained. The substance contained 6% bromine. When the experiment was carried out without the nitrogen flow (dehydrobromination, 6.5 hours), the same results were obtained. A repetition of the experiment with the addition to the reaction mixture of 0.1 ml of dry pyridine resulted in 0.8 g of material with an m.p. of 167-179°. The bromine content was 6.1%. In succeeding experiments, the bromination was carried out under the conditions described above (without the nitrogen flow). 1 g of Δ^{23}-3-keto-24,24-diphenylcholene-3-ethylene ketal (V), 20 ml of carbon tetrachloride, 0.35 g of 99.5% N-bromosuccinimide (5.4% excess), and 0.1 ml of pyridine were used. The dehydrobromination conditions were varied.

b) Dehydrobromination in a mixture of carbon tetrachloride and pyridine (4 : 1). At the end of the bromination and separation of the succinimide, the filtrate was refluxed for five hours, 5 ml of pyridine was then added, and the refluxing was continued for another two hours. The solvent was distilled under vacuum. The tarry precipitate, which still contained a certain amount of pyridine, was washed with alcohol. 0.76 g of a substance with an m.p. of 166-186° was obtained. It contained only traces of bromine. Recrystallization from a mixture of acetone and ethyl acetate (3 : 1) gave 0.456 g of a substance with an m.p. of 188-195°. A second recrystallization increased the m.p. to 193.5-196.5°. The substance was readily soluble in chloroform and difficultly soluble in alcohol, ether, and acetone.

Found %: C 84.92; H 8.82. $C_{38}H_{48}O_2$. Calculated %: C 85.02; H 9.01.

c) Dehydrobromination in glacial acetic acid. After separation of the succinimide and distillation of the carbon tetrachloride under vacuum, 25 ml of glacial acetic acid was added to the residue, and the mixture was refluxed for 20 minutes. The acetic acid was distilled under vacuum, and the tarry residue was dissolved in benzene. The benzene solution was washed with sodium bicarbonate solution and then with water, and the benzene was distilled under vacuum. The remaining material was washed with alcohol. 0.7 g of a substance with an m.p. of 154-179° was obtained. It contained only a trace of bromine.

d) Dehydrobromination by heating in pyridine. The experiment was carried out in 10 ml of pyridine for two hours at 105-110°. The pyridine was distilled under vacuum (30-35°). The remaining tarry material was dissolved in benzene. The benzene solution was washed with dilute hydrochloric acid and water. The residue remaining after distillation of the benzene under vacuum was washed with alcohol. 0.83 g of a substance with an m.p. of 160-180° was obtained. It contained only traces of bromine. Recrystallization from a mixture of acetone and ethyl acetate (3 : 1) increased the m.p. to 190-192°. The weight was 0.39 g.

e) Dehydrobromination in pyridine at room temperature. The experiment was carried out in 15 ml of pyridine for 20 hours at room temperature. Separation of the substance was carried out as described above (d). 0.36 g of a substance with an m.p. of 150-175° was obtained. It contained only a trace of bromine. Recrystallization increased the m.p. to 193.5-196°. The alcohol filtrate was concentrated under vacuum. A dark, tarry substance (0.54 g) remained; it did not evolve hydrogen bromide when heated (refluxed four hours) in carbon tetrachloride. The carbon tetrachloride was distilled under vacuum. The tarry residue solidified when ground with ether. The material was filtered, washed with ether, and dried at 60°. 0.4 g of a substance with an m.p. of 128-132° was obtained. Additional drying at 100° for eight hours did not change the melting point.

Found %: N 1.92; Br 11.5. $C_{43}H_{54}O_2NBr$. Calculated %: N 2.01; Br 11.47.

The substance was readily soluble in alcohol and hot water, and was insoluble in ether. The addition of ether to an alcoholic solution of the material and the cooling of an aqueous solution caused separation of the substance in the form of an oil. The action of silver nitrate on a solution of the substance in aqueous alcohol precipitated silver bromide.

Investigation of the Bromination of Δ^{23}-3-Keto-24,24-diphenylcholene-3-ethylene Ketal (V)

The bromination method was analogous to that described above. 1 g of ketal (V), m.p. 140.5-141.5°, was dissolved in carbon tetrachloride, and the N-bromosuccinimide (99.5%) and 0.1 ml of pyridine were added. The reaction mixture was refluxed under illumination from two lamps (500 W). The reaction conditions were varied.

In all experiments (except experiment 8) the dehydrobromination was carried out under uniform conditions, as described in (b) above. Experiment 8 was carried out by the same method in a mixture of carbon tetrachloride and pyridine (6 : 1). In contrast to the method described previously under (b), separation of the material was carried out after removal of the pyridine by washing with water and a dilute solution of hydrochloric acid. The results of these experiments are presented in Table 1.

Preparation of $\Delta^{20,23}$-3-Keto-24,24-Diphenylcholadiene (VIII)

2 g of $\Delta^{20,23}$-3-keto-24,24-diphenylcholadiene-3-ethylene ketal (VII) was dissolved in 100 ml of dry acetone, 0.1 g of p-toluenesulfonic acid was added, and the mixture was refluxed for 14 hours. Part of the acetone was distilled (about 50 ml), the mixture was diluted with water, and the resulting precipitate was filtered, washed with water to a neutral reaction, and dried at 60°. The substance was recrystallized from acetone. 1.02 g of a substance with an m.p. of 187-190° was obtained. A second recrystallization from acetone and drying under vacuum at 100° increased the melting point to 191-193° (0.83 g). An additional 0.31 g of the substance, m.p. 190-192°, was separated from the filtrate. The substance was readily soluble in chloroform, soluble in ether, and sparingly soluble in alcohol and acetone.

Found %: C 87.95; H 8.83. $C_{36}H_{44}O$. Calculated %: C 87.75; H 9.00.

Preparation of Pregnane-3,20-dione

0.9 g of $\Delta^{20,23}$-3-keto-24,24-diphenylcholadiene (VIII) was oxidized with 0.74 g of chromium trioxide in a mixture of chloroform and 80% acetic acid at 2° and with stirring, which was continued for two hours at 5-10°, and the reaction mixture was then allowed to stand at 10-14° for 15 hours. After the usual treatment, 0.6 g of a tarry substance was separated, washed with hexane and with ether, and recrystallized from aqueous alcohol. The m.p. was 119-121°. A mixture with known pregnane-3,20-dione showed no depression of the melting point.

SUMMARY

The bromination with N-bromosuccinimide of Δ^{23}-3-keto-24,24-diphenylcholene-3-ethylene ketal and the dehydrobromination of the corresponding 22 bromide were investigated.

$\Delta^{20,23}$-3-Keto-24,24-diphenylcholadiene-3-ethylene ketal and $\Delta^{20,23}$-3-keto-24,24-diphenylcholadiene were prepared. The latter was converted to pregnane-3,20-dione.

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A NEW ALKALOID FROM THE CENTRAL ASIATIC LARKSPUR

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The material for our work comprised the underground parts of a larkspur closely related to a known species of mountain larkspur (Delphinium Oreophilum Huth), but differing from it in morphological characteristics. The plant was collected on the VNIKhFI [All-Union Chemical-Pharmaceutical Scientific Research Institute] expedition, under the direction of P.S. Massagetov, in the Aksu-Dzhebogla National Forest in the Southern Kazakhstan District. The original material was collected on August 3, 1954 at an altitude of 1600 meters; the plants were in the flowering phase.

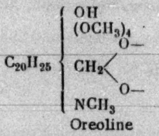
The total bases (0.69% of the weight of dry plant) were extracted with dichloroethane. Paper chromatography established the presence of five alkaloids with R_f 0.35, 0.47, 0.55, 0.68, 0.81.

The present paper describes the separation and investigation of the two alkaloids present in the plants in the greatest amounts, those with R_f 0.47 and 0.55. These alkaloids, which are designated, respectively, (I) and (II), could be separated by virtue of the differing solubilities of the bases and their salts.

Alkaloid (I) had a composition corresponding to the formula $C_{26}H_{43}O_7N$; it contained one OH group, four OCH_3 groups, a methylenedioxy group, and an N-alkyl group, and it did not contain an ester group. The infrared absorption spectrum of base (I) was closely similar to that of lycoctonine; it contained a band characteristic of the OH group in the 3500 cm^{-1} region, and did not contain the carbonyl band.

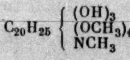
This is a new alkaloid. We propose for it the name oreoline.

After saponification of the methylenedioxy group in oreoline, a substance was obtained with the composition $C_{25}H_{43}O_7N$, which contained three OH groups, four OCH_3 groups, and an N-alkyl group. Bands characteristic of hydroxyl groups were present in the infrared spectrum, while carbonyl bands were absent.



$$C_{20}H_{25}\left\{\begin{array}{l} OH \\ (OCH_3)_4 \\ CH_2\Big\langle\begin{array}{l} O- \\ O- \end{array} \\ NCH_3 \end{array}\right.$$

Oreoline



$$C_{20}H_{25}\left\{\begin{array}{l} (OH)_3 \\ (OCH_3)_4 \\ NCH_3 \end{array}\right.$$

Product from saponification of methylenedioxy group in oreoline

Alkaloid (II) was obtained, in the form of the perchlorate, from the mother liquor remaining from the isolation of the oreoline. This alkaloid was identical with methyllycaconitine.

Work continues on the further investigation of the total alkaloids.

EXPERIMENTAL

Extraction of the alkaloids from the plants. 14 kg of the ground plants was wetted with a 5% solution of sodium carbonate, and was extracted with dichloroethane in a percolation apparatus. The extract was treated with sulfuric acid, and the aqueous layer was agitated twice with ether. The aqueous layer was made alkaline with a 5% solution of sodium carbonate, and was exhaustively extracted with ether and then with chloroform. 77 g of material (Fraction a) was obtained from the ether extract, and 19.5 g of material (Fraction b) was obtained from the chloroform extract. By means of paper chromatography on No. 4 paper (solvent – the upper phase of a mixture of butanol, water and acetic acid taken in the ratio 50 : 50 : 1; time – about 15 hours; temperature – 18-19°; developer – Dragendorff's solution), it was established that Fraction a contained five alkaloids with R_f 0.35, 0.47, 0.55, 0.68, 0.81, and Fraction b contained four alkaloids with R_f 0.36, 0.56, 0.69, 0.82. As may be seen from the R_f values, both the ether and chloroform fractions consisted of the total alkaloids, except for the absence from the chloroform fraction of the substance with an R_f of 0.47, which was completely extracted by ether and which, from the size and intensity of the spot, was the major substance in the total alkaloids.

Isolation of oreoline. 77 g of Fraction a was crystallized from acetone and then twice from alcohol; 6.7 g of oreoline was obtained, m.p. 211-213° (under vacuum), $[\alpha]_D$ −28° (conc. 1.0, chloroform) and $[\alpha]_D$ +55.1° (conc. 1.0, alcohol). The substance was insoluble in water, difficultly soluble in alcohol and acetone, and soluble in ether and chloroform.

Found %: C 64.58; H 8.58; N 3.0; OH 3.45; OCH_3 24.52. $C_{21}H_{28}(OH)(OCH_3)_4(CH_2O_2)N$. Calculated %: C 64.8; H 8.9; N 2.9; OCH_3 25.77; OH 3.53.

An additional 4 g of impure oreoline was obtained by evaporation of the mother liquors.

The hydrochloride of oreoline was prepared by acidification of a solution of the base in anhydrous alcohol with an alcoholic solution of HCl followed by the addition of absolute ether until the solution became turbid; after two crystallizations from alcohol-ether mixture, the m.p. was 186-188°. The substance was readily soluble in water, alcohol, and acetone.

Found %: C 60.68; H 8.4; Cl 6.82. $C_{26}H_{43}O_7N \cdot HCl$. Calculated %: C 60.3; H 8.31; Cl 6.86.

Oreoline perchlorate was prepared by the addition of an aqueous solution of magnesium perchlorate to a solution of the base in 10% HCl. After two recrystallizations of the perchlorate from a mixture of alcohol and ether, the m.p. was 139-142°.

Found %: N 2.33; Cl 6.24. $C_{26}H_{43}O_7N \cdot HClO_4$. Calculated %: N 2.40; Cl 6.02.

Isolation of methyllycaconitine. The mother liquors remaining after the separation of the oreoline were evaporated under vacuum; the residue was dissolved in sulfuric acid; the solution was washed with ether, made alkaline with sodium carbonate, and extracted with ether; 26 g of the amorphous base was obtained. This was dissolved in 10% HCl, and an excess of magnesium perchlorate was added. 7.5 g of the perchlorate was obtained, m.p. 190-194° (from 50% alcohol), $[\alpha]_D$ +27° (conc. 0.4, alcohol). A mixture with a known sample of methyllycaconitine [1] showed no depression of the melting point. From the filtrate remaining after the separation of the methyllycaconitine was obtained 12 g of a mixture of amorphous bases, the separation of which by chromatographing over Al_2O_3 gave a small amount of oreoline and methyllycaconitine.

Saponification of the methylenedioxy group. 5.25 g of oreoline and 3.53 g of phloroglucinol were dissolved in 330 ml of hydrochloric acid (1:1) and heated for two hours at 70-80°. Further treatment was by the method described previously [2]. 2.65 g of the phloroglucide was obtained; this corresponds to a single methylenedioxy group.

From the aqueous solution was isolated 1.7 g of a base with an m.p. of 73-75° (from ether), $[\alpha]_D$ +64.2° (conc. 1.0, alcohol), R_f 0.45 (when chromatographed under the previously described conditions). The substance was insoluble in water, difficultly soluble in ether, and readily soluble in alcohol, acetone, methanol, and chloroform.

Found %: C 64.0; H 8.8; N 3.21; OH 11.75; OCH_3 27.67; NCH_3 5.38. $C_{20}H_{25}(OH)_3(OCH_3)_4NCH_3$. Calculated %: C 63.9; H 9.0; N 2.98; OH 10.87; OCH_3 26.43; NCH_3 6.10.

In view of the close agreement in the analyses, it can be assumed that the nitrogen is bound to a CH_3 group.

A crystalline perchlorate, hydrochloride, oxalate, or picrate could not be prepared. An additional 1 g of the substance was separated from the mother liquor.

SUMMARY

From the mountain larkspur (Delphinium Oreophilum Huth.) was separated 0.69% total bases, the separation of which gave a new alkaloid and also methyllycaconitine.

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PREPARATION OF HYDRATROPIC ALCOHOL

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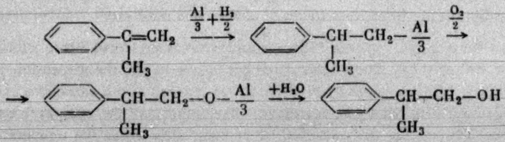
2-Phenyl-1-propanol, or hydratropic alcohol, is of considerable interest as an aromatic principle. This product presently finds application as a "lilac" base in modern perfume compositions [1]. The method used in producing hydratropic alcohol has not been published; however, there is basis for the assumption that its synthesis is accomplished by the reduction of hydratropic aldehyde, which has previously been described in the literature.

Thus, [2] described a process for the reduction of hydratropic aldehyde with activated powdered magnesium in an alcoholic medium; Cohen and co-workers [3], who prepared a series of derivatives of hydratropic alcohol, started with the synthesis of the alcohol from hydratropic aldehyde. Finally, Ramart and Amagat [4] prepared hydratropic alcohol by a multistage synthesis, starting with the nitrile of hydratropic acid and proceeding through the amide, which was reduced with metallic sodium in anhydrous alcohol; along with the hydratropic alcohol, this synthesis also formed the corresponding amine as a by-product. This last method is hardly satisfactory for use in industry. Hydratropic aldehyde, which is a starting material for the preparation of hydratropic alcohol, is, in turn, produced on an industrial scale from acetophenone and esters of monochloroacetic acid through phenylglycidic acid [5]. The multistage nature and the complexity of the methods described above for the synthesis of hydratropic alcohol limit the possibility of using this valuable aromatic principle.

In recent years, Ziegler and co-workers [6] have described in general terms a scheme for the preparation of primary alcohols by oxidation of trialkylaluminums and subsequent hydrolysis of the aluminum alcoholates. For the preparation of the trialkylaluminums, Ziegler used a reaction, discovered by him, between olefins, aluminum, and hydrogen; he has published general information on this reaction in a series of articles [7].

It was very tempting to use the Ziegler reaction for the preparation of hydratropic alcohol (I) according to the scheme presented below.

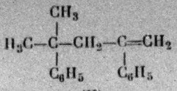


(I)

With synthesis conditions giving good yields, this would be the simplest method and a technically practicable one, since the initial organic component is α-methylstyrene, which is a product of basic organic synthesis.

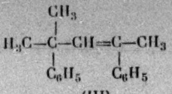
In Ziegler's work [8] on the interaction of olefins, aluminum, and hydrogen, there were indications of the possibility of carrying out the reaction in one stage or in two with the preliminary formation of a dialkylaluminum hydride and subsequent interaction of the latter with the olefin. We confirmed both of these possible variants. Moreover, it was found that the yield of hydratropic alcohol is lower when the reaction is carried out in a single stage owing to the formation of a dimer of α-methylstyrene. In any case, apart from the formation of the dimer of α-methylstyrene, isopropylbenzene is formed, apparently as a result of hydrogenation of the α-methylstyrene in the presence of the heavy metals contained in the aluminum, these metals acting as hydrogenation catalysts.

The fact of the formation of the α-methylstyrene dimer is interesting in connection with the statement by Ziegler [8] that olefins having the isobutylene structure are incapable of polymerizing in the presence of trialkylaluminums. It can be assumed that the structure of the α-methylstyrene dimer obtained in this reaction corresponds to formula (II) and is different from the dimer obtained by Staudinger [9] (III) in the presence of stannic chloride, since in the polymerization of olefins by the Ziegler method, higher olefins with the double bond in the α-position are always formed.



$$H_3C-\overset{CH_3}{\underset{C_6H_5}{C}}-CH_2-\underset{C_6H_5}{C}=CH_2$$

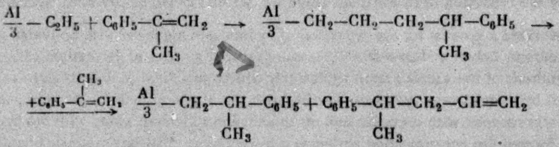
(II)



$$H_3C-\overset{CH_3}{\underset{C_6H_5}{C}}-CH=\underset{C_6H_5}{C}-CH_3$$

(III)

Apart from the compounds indicated, a small amount of 2-phenyl-1-pentene was formed during the synthesis of hydratropic alcohol; we explain the formation of this compound by the interaction of triethylaluminum (used as an activator for the aluminum) and α-methylstyrene with subsequent displacement of the olefin by α-methylstyrene.



$$\frac{Al}{3}-C_2H_5+C_6H_5-\underset{CH_3}{C}=CH_2 \longrightarrow \frac{Al}{3}-CH_2-CH_2-CH_2-\underset{CH_3}{CH}-C_6H_5 \longrightarrow$$

$$\xrightarrow{+C_6H_5-\overset{CH_3}{C}=CH_2} \frac{Al}{3}-CH_2-\underset{CH_3}{CH}-C_6H_5+C_6H_5-\underset{CH_3}{CH}-CH_2-CH=CH_2$$

When the interaction of α-methylstyrene, aluminum, and hydrogen is carried out in two stages, practically no α-methylstyrene dimer is formed; the yield of hydratropic alcohol in this case amounts to 55% calculated on the α-methylstyrene.

EXPERIMENTAL

The α-methylstyrene was prepared by dehydration of dimethylphenylcarbinol at atmospheric pressure over anhydrous aluminum oxide in the presence of iodine. The crude product was washed with an aqueous solution of sodium hydroxide, dried with potassium carbonate, and distilled in a column over metallic sodium. A product was obtained with a b.p. of 161°, n_D^{25} 1.5325; the literature values are 161-162°, n_D^{17} 1.5330 [10]. The finely divided aluminum (1-5 μ particle size) was used as a suspension in gasoline range hydrocarbons (b.p. 95-105°). Triethylaluminum (2-5% by weight of the total charge) was used to activate the aluminum. The hydrogen used in the synthesis was preliminarily freed from traces of oxygen and moisture.

The experiments were carried out in a 1-liter, stainless steel autoclave fitted with a stirrer, a manometer, and an electric heater. When the synthesis was carried out in two stages, the suspension of aluminum and triethylaluminum (74% solution in gasoline-range hydrocarbons) was charged to the autoclave under a stream of oxygen-free nitrogen. Hydrogen was then fed to the autoclave. The contents of the autoclave were heated to 80° with the stirrer in operation. The heating was continued for an hour, after which the temperature was lowered to 50°, and the α-methylstyrene was charged. The reaction mixture was heated to 140°. When this temperature was reached, the pressure dropped sharply (from 80 to 35 atm) over a period of several minutes, after which it was restored to the original value with hydrogen. The process was stopped when no further pressure drop was observed. The entire synthesis required about two hours counting the time from after the charging of the α-methylstyrene.

When the reaction was carried out in a single stage, all components were charged simultaneously, after which hydrogen was charged to the reactor and the stirrer and heater were switched on. In this case, the pressure began to drop when the temperature reached 95°; the absorption of hydrogen ceased at 120-130°.

The oxidation was carried out in a conical flask fitted with a stirrer, a thermometer (submerged in the liquid), a reflux condenser, and a tube extending almost to the bottom of the flask for the introduction of dry air (or oxygen). The process proceeded with the evolution of heat; the temperature was maintained at not above 70° by controlling the air feed rate and the rate of stirring. After the temperature decrease occurring during the feeding of air, the oxidation was completed with oxygen; with the introduction of the oxygen, there was first observed a rise in temperature followed by a rapid decrease to room temperature, after which the feeding of oxygen was continued for another hour. Since excess aluminum was introduced into the reaction, aluminum was always present in the reaction mixture removed from the autoclave; experiments showed that the presence of aluminum had no effect on the oxidation process.*

The hydrolysis was carried out with 10-15% hydrochloric acid while stirring. The order of addition of the reagents had no effect. If the reaction mixture contained aluminum after the oxidation, a larger amount of hydrochloric acid was required for complete solution. After hydrolysis of the reaction mixture, the oil layer was separated from the lower, aqueous layer. The latter was extracted with ether (2-3 times with 50-ml portions). The ether extracts were combined with the oil layer, and the solution was washed with a solution of sodium carbonate or potassium carbonate, dried with potassium carbonate, and distilled in a column. The results of the experiments on the preparation of hydratropic alcohol are presented below.

1. The single-stage reaction of α-methylstyrene, aluminum, and hydrogen. 300 g of α-methylstyrene, 50 g of aluminum, 250 g of gasoline-range hydrocarbons, and 25 g of 74% triethylaluminum were charged to the autoclave. The initial hydrogen pressure was 50 atm. The pressure began to drop when a temperature of 95° (85 atm) was reached, and it continued to drop over a period of three hours (highest temperature was 130°). 515 g of reaction mixture was used in the oxidation. After hydrolysis of the oxidation product and distillation of the solvents (ether and gasoline hydrocarbons), the mixture was vacuum distilled. Four fractions were obtained.

The first fraction (88 g) was isopropylbenzene.

B.p. 29-30° at 8 mm, n_D^{20} 1.4928. Literature data: b.p. 26.8° at 5 mm [11], n_D^{20} 1.4930 [12].

The second fraction was 2-phenyl-1-pentene (12 g).

B.p. 40-50° at 5 mm, n_D^{25} 1.5054, d_4^{25} 0.8684, MR_D 49.96; calc. 48.92; bromine number 106.2; calc. 109.3.

The third fraction was hydratropic alcohol (93 g; 33% yield calculated on the α-methylstyrene).

B.p. 85° at 3 mm, n_D^{26} 1.5225, d_4^{26} 1.00, MR_D 41.60; calc. 41.68. According to literature [1]: b.p. 114° at 14 mm, n_D 1.5262, d 1.01.

Found %: C 79.17; H 9.40. $C_9H_{12}O$. Calculated %: C 79.36; H 8.88.

The phenylurethan of the hydratropic alcohol had an m.p. of 54-56°.

Found %: C 75.01; H 6.69; N 5.75. $C_{16}H_{17}O_2N$. Calculated %: C 75.28; H 6.69; N 5.48.

The fourth fraction was a dimer of α-methylstyrene (47 g).

B.p. 170-175° at 8 mm, n_D^{25} 1.5636, d_4^{25} 0.9850, MR_D 77.96; calc. 77.65 (for 4-methyl-2,4-diphenyl-1-pentene, II).** Bromine number 65.1; calc. 67.6.

According to [13]: for the dimer of α-methylstyrene, b.p. 166-167° at 10 mm, d_4^{25} 0.9850, n_D^{25} 1.5636.

Found %: C 89.67; H 8.52. $C_{18}H_{20}$. Calculated %: C 91.50; H 8.55.

2. The two-stage reaction of α-methylstyrene, aluminum, and hydrogen was carried out as indicated above. 50 g of aluminum in 250 g of gasoline-range hydrocarbons and 5 ml of 74% triethylaluminum were used in the reaction. 154 g of α-methylstyrene was added at the end of the first stage of the reaction. When a temperature of 140° was reached, the pressure dropped to 35 atm over a period of one hour and fifteen minutes. 400 g of reaction mixture was discharged from the autoclave. After the oxidation and hydrolysis, the reaction products were distilled. Fractions identified as in the preceding case were obtained. The yield of hydratropic alcohol by this method was 55% calculated on α-methylstyrene.

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*When required, the aluminum could be filtered in a stream of dry, oxygen-free nitrogen. The unreacted aluminum could be used in a subsequent synthesis.

**For the α-methylstyrene dimer prepared by Staudinger [9], namely, 2-methyl-2,4-diphenyl-3-pentene (III): b.p. 118-120° at 0.1 mm, d_4^{20} 1.0038, n_D^{20} 1.5633, MR_D 76.29; calc. 77.65.

SUMMARY

1. The synthesis of hydratropic alcohol from α-methylstyrene through organoaluminum compounds was carried out with a yield of 55%. The simplicity of the preparation of the alcohol from available starting materials makes this method the simplest for industrial use.

2. The composition of the by-products formed during the synthesis of hydratropic alcohol was investigated; an explanation of the mechanism of their formation was given.

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ELECTROSYNTHESIS OF NICOTINIC ACID

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There has appeared in the literature only a very small amount of work devoted to the electrolytic oxidation of β-picoline to nicotinic acid and of quinoline to quinolinic acid (the latter is readily decarboxylated to nicotinic acid). Thus, an attempt to oxidize electrolytically α-, β-, and γ-picolines to the corresponding aldehydes resulted in low yields [1]. The electrolytic oxidation of β-picoline in 30% sulfuric acid to nicotinic acid and of quinoline in 75-80% sulfuric acid to quinolinic acid has been accomplished [2]. According to other data [3], the oxidation of quinoline should be carried out in 40% sulfuric acid. Attempts at the electrosynthesis of nicotinic acid from nicotine [4], anabasine [5, 6], and N-methylanabasine [5] have been described.

An electrochemical method for the preparation of nicotinic and quinolinic acids is of great interest, since it does not involve the use of oxidizing agents and catalysts. However, the data available in the literature are insufficient for practical use of this method.

In the present work on the electrolytic oxidation of β-picoline, we studied the effect of the quantity of electricity passed through the electrolyte, the current density, the temperature, the addition of Mn^{++} and Cr^{+++}, and the concentration of β-picoline and of sulfuric acid on the yield (B) of nicotinic acid and on the current efficiency (A). The effect of the electrolysis conditions on the rate of oxidation of β-picoline and nicotinic acid was also studied.

In addition, the effect of the concentration of sulfuric acid and of quinoline on the yield of nicotinic acid in the electrolytic oxidation of quinoline was studied.

EXPERIMENTAL

Method. The following method was used for the preparation of pure β-picoline. The nonbasic impurities were steam-distilled from a picoline fraction (b.p. 138-144°) acidified with sulfuric acid. The free bases were made alkaline, and the β-picoline was then separated in the form of the difficultly soluble salt $CuSO_4 \cdot 5H_2O \cdot 2C_6H_7N$ [7]. β-Picoline of 98-99.5% purity was obtained by threefold recrystallization by cooling; the purity was determined by the freezing point method [8].

The experiments on the electrosynthesis of nicotinic acid were mainly carried out using a lead anode in sulfuric acid solution. It was also possible to use a platinum anode with the same solution, but the yield of nicotinic acid was somewhat less. Magnetite and graphite anodes in acid medium and also platinum, iron, and nickel anodes in alkaline medium were inactive.

The electrolytic cell was an 0.5-liter beaker 130 mm in diameter and 75 mm high, inside of which was placed a ceramic diaphragm 58 mm in diameter and 145 mm high and impregnated with water glass to decrease the permeability [9]. A cylindrical anode (2 sq. dm. surface area), prepared from sheet lead, surrounded the diaphragm. The volume of anolyte was ~50 ml. The volumetric current density in the anolyte varied up to 1000 amp/liter. The lead cathode (1 sq. dm. surface area) was inside the diaphragm in the beaker. The catholyte was 10-20% sulfuric acid. The cell was placed in a thermostatted bath. At the conclusion of an experiment, the anolyte was filtered free from slime, neutralized with sodium carbonate, then acidified with acetic acid to a pH of 4-4.5, and heated on a boiling-water bath. Copper sulfate or acetate was added to the hot solution, and the heating was continued for an additional several hours. The resulting precipitate of copper nicotinate was determined gravimetrically. The yield of nicotinic acid was calculated from the amount of copper nicotinate and was based on the weight of the original β-picoline. In order to isolate the nicotinic acid, the copper salt was treated with a solution of sodium sulfide, the copper sulfide was filtered, and the free nicotinic acid was precipitated (pH 3.3) by acidification of the filtrate with hydrochloric acid. Loss during the separation was ~10%.

Oxidation of quinoline and separation of the quinolinic acid as the copper salt were carried out similarly. In the experiments on the oxidation of quinoline, the amount of electricity passed was 28 F/mole of the initial material, i.e., 155% of that calculated from the reaction

$$C_9H_7N + 9[O] \rightarrow C_5H_3N(COOH)_2 + 2CO_2 + H_2O$$

Electrolytic oxidation of β-picoline. The effect of the quantity of electricity passed through the electrolyte (Q*) on the current efficiency (Curve 1) and on the yield (Curve 2) is shown in Fig. 1. The experiments were carried out under the following conditions: temperature, 40°; anode current density, 10 amp/dm^2; anolyte, 1 M solution of β-picoline in 7 N sulfuric acid.

The low current efficiency observed at the beginning of the electrolysis (Fig. 1) indicates the formation of intermediate products of the oxidation of β-picoline, apparently pyridine-3-carboxaldehyde, which is in agreement with the literature [1]. The maximum yield of nicotinic acid (52-54%) was obtained when 150-200% of the theoretical amount of electricity had been charged. When Q exceeded 200%, practically no β-picoline remained in the anolyte.

As follows from the graphs of the data, the nicotinic acid formed as a result of oxidation of β-picoline is rather easily oxidized further. However, the oxidation of β-picoline proceeds at a considerably greater rate, owing to which it is possible to obtain nicotinic acid in rather high yield. Specially conducted experiments on the electrolytic oxidation of nicotinic acid (Table 1) permit a comparison of the over-all current efficiencies during the electrolytic oxidation of β-picoline and nicotinic acid.

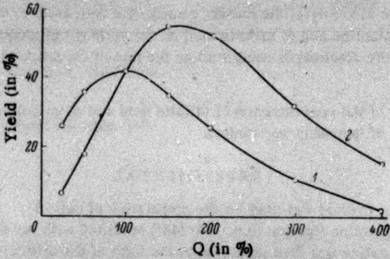

Fig. 1. Variation in yield of nicotinic acid with quantity of electricity passed: 1) current efficiency; 2) yield.

The over-all current efficiency for all oxidation products was determined from the volume of oxygen evolved during electrolysis of a sulfuric acid solution of β-picoline or nicotinic acid (v_1) as compared to the volume of oxygen evolved in the same time from a solution of pure sulfuric acid of the same concentration (v_2). The fraction of the current consumed in the oxidation of the organic substances is:

$$A_1 = \frac{v_2 - v_1}{v_2},$$

---

*A Q of 100% corresponds to the theoretical amount (6 F/mole).

TABLE 1

Concentration of β-picoline or nicotinic acid (M)	Over-all current efficiency for all oxidation products (in %) during oxidation of	
	β-picoline	nicotinic acid
0.01	15	0
0.1	62	11
1.0	94	43

Note: Experimental conditions: temperature, 40°; current density, 5 amp/dm^2; sulfuric acid concentration, 7.5 N.

In a study of the effect of anolyte temperature, it was found that the maximum yield is obtained at 30-40° (Table 2). The decrease in the yield of nicotinic acid with an increase in temperature above 40° is apparently due to acceleration of the side reactions, since the over-all rate of all oxidation processes was almost unchanged with the increase in temperature.

TABLE 2

Q (in %)	Yield (in %) at an anolyte temperature of				
	20°	30°	40°	60°	80°
50	15	–	21.5	–	–
100	39	–	41	38	36
150	45	53	54	42	37
200	48	54	54	47	35
250	44	48	46	–	–

Note: Experimental conditions: current density, 5 amp per dm^2; sulfuric acid concentration, 3.5 N; β-picoline concentration, 1 M.

A change in the anode current density within the limits of 1-10 amp/dm^2 had little effect on the yield of nicotinic acid (Table 3). Nor did the introduction of small amounts of Mn^{++} and Cr^{+++} have an appreciable effect (under the experimental conditions of Table 3 at a current density of 5 amp/dm^2).

TABLE 3

Q (in %)	Yield (in %) at an anode current density of (in amp/dm^2)			
	1	3	5	10
50	25	23	21.5	18
100	47	43	41	42
150	56	56	54	55
200	51	50	54	53
250	45	48	46	48

Note: Experimental conditions: temperature, 40°; β-picoline concentration, 1 M; sulfuric acid concentration, 7 N.

A change in the acidity of the anolyte within the limits of 11 to 17 N had almost no effect on the yield (Fig. 2). An increase in the initial concentration of sulfuric acid to 25 N led to a decrease in the yield to 32-34%

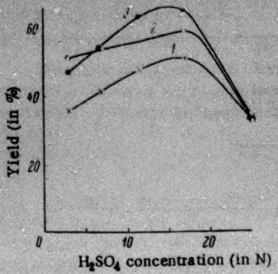

Fig. 2. Variation in the yield of nicotinic acid with concentration of sulfuric acid in the anolyte. (Concentration of β-picoline, 1 M; temperature, 40°; current density, 5 amp/dm^2.) Values of Q (in %): 1) 100; 2) 200; 3) 150.

as a result of considerable corrosion of the anode during the electrolysis.

An increase in the acidity of the anolyte during electrolysis owing to the passage of electricity was proportional to the quantity of electricity passed; therefore, during the study of the effect of the concentration of β-picoline, the initial concentration of sulfuric acid was chosen so that the average acidity during the electrolysis was approximately the same in all experiments and remained within the limits corresponding to maximum yield of nicotinic acid (Table 4).

From the data presented, it follows that the electrolytic oxidation of β-picoline to nicotinic acid can be successfully carried out under a wide range of electrolysis conditions, the yield of nicotinic acid reaching 65% at a current efficiency of 43% under the same conditions. When the process is carried out on a larger scale, it is possible that it will be more expedient to produce nicotinic acid at maximum current efficiency (55%), passing 100% of the theoretical amount of electricity rather than 150-200%, and to extract the unoxidized β-picoline from the solution after electrolysis.

TABLE 4

Q (in %)	Yield of nicotinic acid (in %) at concentrations of					
	β-picoline, 1 M	sulfuric acid, 17 N	β-picoline, 1.7 M	sulfuric acid, 15.5 N	β-picoline, 3.5 M	sulfuric acid, 13 N
100	51		55		49	
150	65		65		57	
200	59		59		44	

Note: Experimental conditions: temperature, 40°; current density, 5 amp/dm^2.

TABLE 5

Sulfuric acid concentration (in %)	25	38	52	65	75
Yield of quinolinic acid (%)	Trace	40	50	54	59

Note: Experimental conditions: temperature, 70-75°; current density, 2 amp/dm^2; quinoline concentration, 100 g/liter.

TABLE 6

Quinoline concentration (in g/liter)	7	35	70	100	140
Yield of quinolinic acid (in %)	32	47	52	59	58

Note: Experimental conditions: temperature, 70-75°; current density, 2 amp/dm^2; sulfuric acid concentration, 75%.

Electrolytic oxidation of quinoline. During the oxidation of quinoline, a change in the anode current density from 1 to 4 amp/dm^2 had no substantial effect on the yield of quinolinic acid. Electrolysis at higher current densities led to a significant increase in the volume of the anolyte owing to considerable gas formation. In experiments carried out at room temperature, the solution contained a considerable amount of tar after the electrolysis; it was not possible to separate the quinolinic acid. Better results (yields up to 60%) were obtained at an anolyte temperature of 78-80°. A further increase in the temperature led to a decrease in the yield. The electrolytic oxidation of quinoline to quinolinic acid proceeds not only in 65-75%, but also in 40-50% sulfuric acid (Table 5), although, according to the data of M. Kulka [2], quinolinic acid is not formed in solutions with a sulfuric acid concentration of 50% or less.

During the study of the effect of quinoline concentration on the yield of quinolinic acid, it was found that the optimum concentration is 100-140 g/liter (Table 6); this is approximately one-third the concentration recommended in [2].

An advantage of the oxidation of quinoline in 40-50% sulfuric acid, with a quinolinic acid yield of 40-50% and a current efficiency of 20-25%, is the considerably less anode corrosion under these conditions. Concentrated solutions of quinoline foam strongly during electrolysis.

SUMMARY

1. The electrolytic oxidation of β-picoline to picolinic acid was investigated with respect to the effect of solution composition and electrolysis conditions.

2. It was established that nicotinic acid can be obtained at a maximum current efficiency of 55%; the maximum yield was 65%.

3. It was found that nicotinic acid is oxidized electrolytically, but with greater difficulty than β-picoline.

4. It was shown that it is possible to oxidize quinoline electrolytically to quinolinic acid at a lead anode with a yield of up to 60%.

5. The electrochemical method for the preparation of nicotinic and quinolinic acids can be recommended for practical use.

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DISCUSSION SERIES

CONJUGATION IN, AND THE DUAL REACTIVITY OF, BUTADIENE

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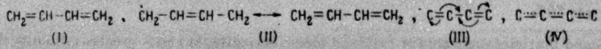
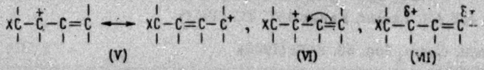
1. In one widely accepted chemical theory, the dual reactivity of π-conjugated systems is explained by a mesomeric structure of these molecules both in their natural state and in the form of carbonium ions formed during the course of the reaction. According to this theory, the 1,3-butadiene molecule, owing to the mesomeric effect (in other terms – the effect of static conjugation), cannot be represented by the usual classical structural formula with alternating double and single bonds (I), but only by formulas of the type of (II), (III), and (IV).



$CH_2{=}CH{-}CH{=}CH_2$ (I), $\dot{C}H_2{-}CH{=}CH{-}CH_2 \longleftrightarrow CH_2{=}CH{-}CH{=}CH_2$ (II), $C{=}C{-}C{=}C$ (III), $C{\cdots}C{\cdots}C{\cdots}C$ (IV)

Formulas (II-IV) express the assumption of the equalization of the bonds in 1,3-butadiene, both with respect to the distribution of π-electron density [1] and with respect to the ratios of bond lengths [2]. According to this theory, it is precisely this mesomeric structure of 1,3-butadiene which leads to a concentration of the electron density at the 1 and 4 atoms, and thereby creates conditions favorable for the approach of an electrophilic reagent to these atoms; the resulting mesomeric carbonium ion also has a mesomeric structure (V-VII) – its positive charge "is not localized at the second carbon atom" [3], but is distributed along the bonds



$XC{-}\overset{+}{C}{-}C{=}C \longleftrightarrow XC{-}C{=}C{-}C^{+}$ (V), $XC{-}\overset{+}{C}{-}C{=}C$ (VI), $XC{-}\overset{\delta+}{C}{-}C{=}\overset{\delta+}{C}$ (VII)

Owing to this, in the second stage of the reaction, the anion of the reagent "can attack both the second and the fourth carbon atoms" [3], thereby exhibiting the dual reactivity of such compounds [4-6].

2. As confirmation by direct physical experiment, the authors of this theory attempted to assemble the experimental data on interatomic distances through a comparison of the lengths of double and single bonds in π-conjugated systems, on the one hand, and in ethylene and ethane as standards, on the other*; they attempted to establish an equality of the lengths of the bonds in π-conjugated systems and to establish thereby their mesomeric structure [7]. However, a more detailed consideration of the experimental material shows the complete incompetence of such an illustration. Actually, it is an undoubted experimental fact that the interatomic distance of the single C—C bond in 1,3-butadiene (1.46±0.03 A [8]) is shortened in comparison with the C—C bond in ethane (1.55±0.03 A [9]). The difference in the available results of experimental measurements of the interatomic distance in the C=C bonds in 1,3-butadiene (1.35±0.02 A [3]) and ethylene (1.353±0.001 A [10], 1.34±0.02 A [9], 1.33 A [10]) lies within the limits of experimental error, and, in any case, does not permit the conclusion as to the lengthening of the double bonds in 1,3-butadiene.** Electron diffraction measurements of the lengths of the

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*See [1], p. 38.

**We note that in another paper [11], the author of [2], cited above, was himself forced to state that, according to the available measurements, lengthening of the double bonds in 1,3-butadiene as compared to ethylene "lies within the limits of experimental error, and, therefore, it is impossible to base on them any substantial conclusions as to the structure of conjugated systems."

C≡C bonds in diacetylene ($HC\equiv C-C\equiv CH$ 1.19±0.03 A [12]), dimethyldiacetylene ($H_3CC\equiv C-C\equiv CCH_3$ 1.20± ±0.02 A [12]), diphenyldiacetylene ($H_5C_6-C\equiv C-C\equiv C-C_6H_5$ 1.18 A [11]), and other acetylenes indicate, rather, the shortening of these bonds as compared to the length of the C≡C bond in acetylene (1.205±0.008 A), but in any case, they do not indicate lengthening of these bonds. The x-ray data available at the present time on the lengths of multiple bonds in π-conjugated systems also indicate no lengthening of these bonds. Thus, in one of the monograph collections on x-ray analysis of organic compounds, it is stated that the length of the C≡C bond in tolane is 1.19 A, and in stilbene the length of the C=C bond is 1.33 A, that is, "not lengthened, which is in complete agreement with the situation found in other conjugated systems" [13].

As we have shown in previous work [14-16], at the present time opinions as to the changes in lengths of characteristic bonds can be formed with greater accuracy from their vibrational frequencies than from measurements of their lengths. In fact, an increase in the interatomic distance of a characteristic bond correlates strictly with the decrease in the vibrational frequency and the decrease in bond energy, while an increase in vibrational frequency and bond energy correlate with a decrease in bond length. At the present-day level of measuring techniques, the measurement of the vibrational frequency of bonds in molecules is carried out with enormously greater accuracy and ease than the measurement of the other two parameters mentioned above. This is especially important for C=C and C≡C bonds, since in these bonds (especially in the latter) the carbon atoms are already very close together, and their further approach is hindered by forces of repulsion which increase strongly at short distances. As a result, the curves of the vibrational frequencies of C=C and C≡C bonds rise sharply with an increase in interatomic distance; i.e., the significant increase in the vibrational frequencies of these bonds (especially the C≡C bond), which is readily established experimentally, corresponds to a quite insignificant reduction in interatomic distance, the direct measurement of which at the present-day level of technique of the appropriate measurements becomes lost in the limits of experimental error.

The presence in 1,3-butadiene and diacetylene of two multiple bonds leads to a splitting of their vibrational frequencies into two frequencies (mechanical effect of splitting of the frequency of coupled vibrations), one of which (the symmetric vibration) appears in Raman spectra and the other of which (the antisymmetric vibration) appears in infrared spectra. Let us turn first to data from Raman spectroscopy.

In conformity with the above, data from the Raman spectrum of 1,3-butadiene indicate a shortening of the C=C interatomic distance in comparison with ethylene: the characteristic frequency of the symmetric vibration of the C=C bonds in 1,3-butadiene (1638 cm^{-1})* is substantially higher than the vibrational frequency of the C=C bond in ethylene (1621 cm^{-1})**; this increase lies outside the limits of experimental error.

1,3-Butadiene can be considered as a mono-substituted ethylene. Among the possible substituents, there are those (the chlorine atom, etc.) which decrease the vibrational frequency of the double bond in ethylene, simultaneously increasing the interatomic distance; others (the methyl group, ethyl group, etc.) increase the vibrational frequency of the double bond in ethylene, simultaneously shortening the interatomic distance. From the frequency of the symmetric vibration of the double bond, 1,3-butadiene belongs to the second group of monosubstituted ethylenes:

	rA (C=C)	$\Delta\nu$ cm^{-1} (C=C) [17]
Ethylene	1.353 [9]	1621,
Vinylchloride.	1.380 [18]	1601,
Methylethylene. . . .	–	1648,
Ethylethylene.	–	1639,
1,3-Butadiene.	1.350 [8]	1638.

To still a greater degree than in 1,3-butadiene, this same thing appears in diacetylene. Along with a sharp decrease in the length of the single C−C bond (1.36±0.03 A) [12], the interatomic distance of the C≡C bond is also certainly shortened, as indicated by the very significant increase in the frequency of the symmetric vibration of these bonds as compared to the frequency of C≡C in acetylene (by 218 cm^{-1}!).

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*The Raman spectrum of 1,3-butadiene, which exists predominately in the trans-form, was taken in solution in cyclohexane with a domestic ISP-51 spectrograph with a standard camera using the excited line from a mercury lamp at 4358 A; $\Delta\gamma$ (cm^{-1}): 515 (4), 891 (1), 905 (1), 1014 (1), 1201 (4), 1309 (2), 1431 (4), 1638 (10), 3003 (6), 3087 (1).

**Liquid ethylene.

If diacetylene is considered as a substituted acetylene, without any doubt it does not belong to that group of these compounds in which the substituent decreases the vibrational frequency and increases the interatomic distance of the C≡C bond (chlorine in chloroacetylene), but, on the contrary, it belongs to that group in which the substituent increases the vibrational frequency and shortens the interatomic distance, the effect being greater than that caused by the methyl group in methylacetylene:

	rÅ (C≡C)	$\Delta\nu$ cm^{-1} (C≡C) [17]
Acetylene	1.205 [10]	1965,
Chloroacetylene	1.210 [18]	– ,
Methylacetylene	1.200 [19]	2125,
Diacetylene	1.190 [12]	2183.

Thus, in the π-conjugated systems under consideration, in the symmetrical vibrational states of the multiple bonds there is a shortening of the interatomic distances. Conjugation, in this case, leads to a contraction of the molecular skeleton owing to the decrease in the lengths of both the single and the multiple bonds.

The frequency of the nonsymmetric vibration of the C≡C bond in diacetylene, which appears in the infrared spectrum (2085 cm^{-1}) [17], also considerably exceeds the frequency of the C≡C vibration in acetylene; the frequency of the nonsymmetric vibration of the C=C bonds in 1,3-butadiene is somewhat lower (1603 cm^{-1} [20]) than in ethylene. The average of the multiple-bond frequencies for the two vibrational states (symmetric and antisymmetric – 2134 cm^{-1}) indicates that in diacetylene the averaged, with respect to vibrational state, multiple bond* is shortened in comparison with the C≡C bond in acetylene; in 1,3-butadiene (1620 cm^{-1}), the averaged multiple bond is on a par with ethylene, and, in no case, is it lengthened in comparison with the double bond in ethylene.

We may point out that, together with A.D. Matveeva, we have investigated the Raman spectrum of hexachlorobutadiene, and in this spectrum there appear both symmetric (1611 cm^{-1}) and antisymmetric (1566 cm^{-1}) vibrations for the multiple bonds. The averaged frequency of these vibrations (1589 cm^{-1}) substantially exceeds the frequency of the vibration of the double bond in tetrachloroethylene (1571 cm^{-1}); i.e., in this compound the averaged length of the multiple bond is shorter than the ethylenic bond in tetrachloroethylene.

In previous work [14-16], we showed that an accurate optical experiment decisively refutes the hypothetical mesomeric-resonance theory with respect to certain mutual effects of the atoms in molecules, hyperconjugation of the first and second orders (σ,π- and σ,σ-conjugation), nor are the electronic shifts proposed by this theory in any way real. As seen from the material presented above, an accurate optical experiment also refutes the hypothetical mesomeric-resonance theory of conjugation (the mesomeric effect or effect of static conjugation, π,π-conjugation), showing that the electronic shifts proposed by this theory, which lead to mesomeric equalization of the bond lengths (including a lengthening of the multiple bonds) and, in addition, to an equalization of the electron densities of the bonds, are not real.**

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*These averaged bond lengths are measured in x-ray and other investigations.

**In this theory, equalization of the electron density along the bonds is explained by geometrical considerations and certain mathematical operations, and, as emphasized by the authors themselves, this explanation is rough, qualitative, and very simplified, and, moreover, it is devoid of physical meaning [21]. More precisely, the theory maintains that in a conjugated system of π-bonds, the dumbbell ("figure-eight" type) of "p-orbital of the central C_2 atom overlaps to an equal degree the p-orbitals of each of the neighboring atoms" [22], which is also presumed to lead to equalization of the electron density along the bonds (for an illustration of the overlapping of p-orbitals, see [22]). The very history of the emergence, without basis, of these "dumbbells" ("figure-eights") in the presently considered theory indicates the incompetence of the concepts of this nature of the Copenhagen school of quantum mechanics in theoretical chemistry. As is well known, the "figure-eight" appeared as a graphical representation of the results of simplified evaluations of only the second of three terms in the expression for the probability of finding the single valence electron of hydrogen and hydrogen-like atoms in the p-state in the vicinity of the nucleus ($P=\psi\bar{\psi}dV=\Phi_m\bar{\Phi}_m\cdot[\vartheta_{ml}]^2\cdot[R_{nl}]^2$); this term characterizes the indicated probability in

(Footnote continued on next page)

3. Contraction of molecules with conjugated bonds occurs owing to interaction of pairs of π-electrons (through interaction of their electromagnetic and other fields) localized in the 1,2-, 3,4- and other bonds. Two facts indicate the presence of this interaction and its distribution along the entire system of conjugated bonds: 1) a shift in the ultraviolet absorption bands toward longer wavelengths with an increase in the units in the polymethylene chain, the large number of interacting π-electrons involved in the transition from ethylene to a polymethylene chain (ethylene – 193, 1,3-butadiene – 217, hexatriene – 258, and octatriene – 286 mμ [25]) having an effect on this shift; 2) the lack of free rotation around the C–C single bond. One of the clearest proofs of the fact that contraction of a conjugated molecular system occurs through the direct interaction of pairs of π-electrons localized in 1,2-, 3,4-, etc. bonds is the structure of diacetylene. The contraction in diacetylene of the C–C distance to the interatomic distance in C=C double bonds (1.36 A [12]) is not accompanied by the appearance of a vibrational frequency in the region characteristic for it, since possession of another pair of electrons at the 2,3-atoms is required for the appearance of this frequency (i.e., an additional force interaction). This requirement is not met, since the two pairs of π-electrons are localized in the 1,2- and 3,4-bonds, thereby providing for the full-valued acetylenic character of these bonds and making them even shorter and stronger, as we have seen. Acting as though "from without," the interacting pairs of π-electrons localized in the 1,2- and 3,4-bonds draw together the atoms in the C–C bond to a distance of 1.36 A (instead of 1.55 A) without converting this bond to a multiple bond (double); the force constants of the central C–C single bond in diacetylene (as in dimethyldiacetylene), calculated taking into account its vibrational frequency, are significantly (more than 20%) lower than for ethane [26]. A similar picture holds for 1,3-butadiene and other conjugated systems.

4. Understanding of the dual reactivity of 1,3-butadiene must come from an understanding of its real structure as characterized above and from the dynamic concepts relative to the nature of the molecule, as developed in the theory of chemical structure by A.M. Butlerov and also by V.V. Markovnikov and M.A. Il'inskii.*

The most electronized regions in 1,3-butadiene [14-16] are the regions of the double bonds, and the most electronized locales in these regions are the 1- and 4-carbon atoms, which are in methylene, not methyne, groups, as indicated by the high vibrational frequencies of the methylene groups, particularly in their antisymmetric vibrational state.**

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terms of only one polar coordinate – the angle ϑ (the "latitude"). Specific characteristics of this case are spherical symmetry of the field, one valence electron, and the absence of the action of an external field. But, at the beginning of the 1930's, in the theory under consideration, the "figure-eight" was transferred arbitrarily [23] to the *p* electrons of the carbon atom and, moreover, to carbon atoms in molecules with π-bonds; i.e., the "figure-eight" was extended to the case in which all of the most important conditions for its occurrence (spherical symmetry, etc.) are completely absent. The question became merely how to dispose this "figure-eight" in the coordinate system to obtain the desired calculated results – minimum energy of the system. It developed that for this purpose, the axes of the "figure-eights" had to be parallel to each other, perpendicular to the line of the bond between carbon atoms; in π-conjugated systems, the p-orbital of the central atom must equally overlap with the p-orbitals of the neighboring atoms [22]; all of this mathematically guarantees the maximum value of the exchange integral (overlap integral) and, thereby, a minimum value of the energy of the system [24]. Such an arbitrary transfer of a simplified, single-coordinate, mathematical scheme of the electron density of hydrogen and hydrogen-like atoms with their spherically symmetrical fields to complicated molecular systems with the further arbitrary mathematical assumptions for the purpose of obtaining a calculated minimum energy for the system in no way reflects physical reality, nor does it rest on any physical experiment, and it is disproved by the other experimental, physical data cited above.

*With this "dynamic point of view of the nature of a chemical compound" [27, 28] (cf. [15, 16]), A.M. Butlerov discovered the phenomenon of tautomerism, and he explained by it the dual reactivity of various compounds [28]. With particular vigor, M.A. Il'inskii developed dynamic concepts regarding molecules (for details, see [29]), and first predicted, on the basis of the theory of chemical structure after its appearance, the existence of free radicals, particularly methyl free radicals. A radical is an independent, internally self-equilibrating, dynamic particle if the radical, as M.A. Il'inskii wrote, "can exist in the free form even though only over the course of an infinitely small time" [30]. These dynamic concepts, which are justified by the entire development of organic chemistry, can clarify for us, in connection with the material presented above, the essence of the mechanism of the reaction occurring during addition to 1,3-butadiene in the 1,2- and 3,4-positions.

**Concerning this, see [14-16, 31].

The frequencies of the methyne and methylene groups are (in cm^{-1}):

	Paraffins*	1,3-Butadiene
CH	2870	3003
CH_2	2853, 2908	3003, 3087

It is natural that the positive end, X, of a molecule of reagent (X is H^+, Cl^+, Br^+, etc.) is directed toward these regions of the molecule; on completion of polarization in the reagent molecules, the positive end adds to one of the terminal atoms of the system with the formation of the ion $XH_2C-\overset{+}{C}H-C=CH_2$. This is the first stage, with respect to time, in the addition reaction. Ionization of the 1,3-butadiene molecule with the formation of a positively charged carbon atom in the 2-position imparts a corresponding impulse to the remaining pair of π-electrons, thereby bringing about the transition of (VIII) to (IX). But the presence in (IX) of a C^+ atom at the end of the chain in turn imparts an impulse to the transition of (IX) to (VIII); i.e., the following tautomerism of the carbonium ions is established:

$$\underset{\text{(VIII)}}{XH_2C-\overset{+}{C}H-CH=CH_2} \rightleftarrows \underset{\text{(IX)}}{XH_2C-CH=CH-\overset{+}{C}H_2}.$$

This definitely involves two tautomeric, separately existing ions which differ in their chemical structure (in the order of the bonds), and not a single mesomeric or hybrid ion [(VIII) $\longleftrightarrow$ (IX) or $XH_2C-CH-CH=CH_2$]. Depending on the reaction conditions, the addition of the negative ion (Cl^-, Br^-) can be to particle (VIII) in the 2-position or to particle (IX) in the 4-position. In order for these reactions to take place, the ions (VIII) and (IX) must be – must exist as – separate particles, though their lifetime be infinitely small. The presence of products of addition at the 1,2- and 1,4-positions is, in turn, proof of the existence of the indicated tautomeric ions as individual particles.

SUMMARY

1. The explanation of the dual reactivity of π-conjugated systems by hypotheses based on the mesomeric effect (static conjugation) in the unreacting molecule and on first order hyperconjugation in the intermediate carbonium ion are not authentic. Such systems (1,3-butadiene, diacetylene, hexachlorobutadiene) do not have mesomeric structures with equalized bonds as proposed by the indicated theory; in particular, their multiple bonds are not lengthened.

2. The first stage of the reaction – polarization of the reagent and the addition of its cation to the end of the molecule – promotes increased electronization of the methylene groups in 1,3-butadiene. The dual reactivity of 1,3-butadiene is brought about by this first stage of the reaction, and is due entirely to the separate existence in space of the ions (VIII) and (IX), which differ in their chemical structures, during the tautomeric transformation of one to the other.

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THERMOGRAPHIC INVESTIGATION OF THE REGENERATION OF CHROMIUM CATALYSTS

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The regeneration of catalysts reversibly poisoned with carbonaceous deposits that shield the active centers consists of burning out these deposits in a current of air or a mixture of various proportions of nitrogen and oxygen. This process has a distinctly exothermic character, and it therefore was expedient to employ for its investigation the method of differential thermal analysis [1].

The question of the relative temperature at which the regeneration process must be carried out is very important; however, the theoretical investigations of this question have been very few. The first work in this direction was that of N. D. Zelenskii and M. B. Turova [2]; from the amount of carbon dioxide that was evolved at different temperatures they judged the degree of contamination of platinum and palladium catalysts by carbonaceous deposits and determined the temperature at which these deposits could be completely removed.

EXPERIMENTAL

The method of recording the thermograms has been described previously [3].

In Fig. 1 are shown the thermograms for a chromium catalyst recorded before and after it had been poisoned in the decomposition of isopropyl alcohol. In the thermogram of the poisoned catalyst the great exothermic effect of the combustion of the carbonaceous deposits is observed, starting at 260°.

Effect of the reaction on the character of the carbonaceous deposits. In Figure 2 are shown the thermograms for a chromium catalyst, obtained by the thermal decomposition of ammonium bichromate (No. 42 in a series of catalysts prepared by us), which was reversibly poisoned in four different reactions: the decomposition of n-propyl alcohol, the decomposition of butyl alcohol, the dehydrogenation of cyclohexane, and the experimental conversion of xylene with steam. In three of the thermograms endothermic effects are observed with minima at about 100-120°, corresponding to the removal of sorbed water, which is a reaction product in the first two instances and one of the starting materials in the last. The exothermic effects in all four thermograms correspond to the combustion of the carbonaceous deposits. The temperatures where these effects start vary within wide limits, from 189 to 580°. This indicates the completely different character of the carbonaceous deposits that had been formed on the catalyst. In the reaction with butyl alcohol, moreover, a part was played by the higher temperature at which the reaction was carried out, which also influenced the character of the deposits, as will be shown below.

The nature of the exothermic effect in thermogram 4 (Fig. 2) of the poisoned chromium catalyst differs from that in the other thermograms. The conversion reaction of xylene with steam, which takes place over Ni on Al_2O_3 [4], did not go with our catalyst, but the latter did sorb a considerable amount of water and was poisoned with carbonaceous deposits.* The exothermic effect of the combustion of these deposits is dichotomous, with maxima at 436 and 496°. This fact provides a basis for supposing that two components are present in the deposits, with different combustion temperatures.

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*From data of A. A. Balandin and T. A. Slovookhotovaia.

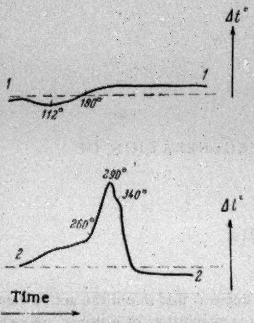

Fig. 1. Thermograms of chromium catalyst: 1) before poisoning; 2) after poisoning.

In Table 1 a comparison is made of the temperatures of the exothermic effects and of the analyses of the carbonaceous deposits for two of the preparations investigated by us.* The comparison of the number of hydrogen atoms on one carbon atom confirms the data of the thermal analysis, which show that the character of the carbonaceous deposits differs, depending on the reaction taking place.

Effect of period of use of the catalyst. In Figure 3 are given three thermograms for a poisoned catalyst which show the effect of the length of time it had been used on the character of the carbonaceous deposits. The decomposition of isopropyl alcohol was carried out on the catalyst at a reaction temperature of 420°. In Table 2 are given the temperatures for the beginning and the maximum of the exothermic effects, the analyses of the carbonaceous deposits, and the loss upon calcination of these samples.

When the period of use of the catalyst without regeneration was increased not only did the amount of carbonaceous deposits increase, as has already been noted previously [5], but the qualitative composition of the coating changed. This is indicated by the change in the character of the thermograms presented in Figure 3, which show the appearance and the increase in amount of the second constituent of the carbonaceous deposits, which has a higher combustion temperature. Actually, in the thermogram of the sample used for 2 hours, only a small inflection is observed at 318°. In the thermogram of the sample used for 6 hours, a bifurcation of the maximum is observed between 283 and 240°, and in the thermogram of the most highly poisoned sample, used for 12 hours, a quite clear dichotomy of the exothermic effect is visible, with maxima at 370 and 475°. This indicates the presence of two constituents in the carbonaceous coating: one that starts to burn at 302°, and the other at about 402°.

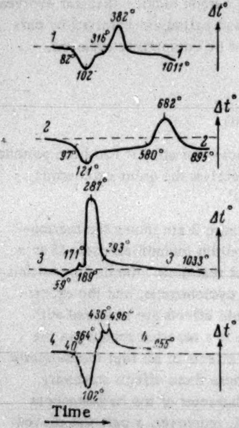

Fig. 2. Thermograms of chromium catalyst poisoned in reactions: 1) decomposition of n-propyl alcohol; 2) decomposition of n-butyl alcohol; 3) decomposition of cyclohexane; 4) conversion of xylene with steam.

With an increase in the period of use of the catalyst, the temperature at which the combustion of the first constituent started was elevated (the initial effect shifted from 240 to 302°). Furthermore, the second, undesirable constituent of this coating, which required a higher regeneration temperature for its removal, made its appearance and grew in importance.

Thermograms of poisoned catalysts recorded in a current of air and in vacuo. The curves 1 and 2 in Fig. 4, correspond to the thermograms of the poisoned catalysts just examined, which were recorded in a current of air; i. e., under the conditions usually employed in carrying out the regeneration process. Comparison of these thermograms with the corresponding thermograms of the same preparations recorded by the usual method in open crucibles (see Fig. 3, curves 1 and 3) shows that the draft of air had considerably less effect on the thermogram of the catalyst used for 2 hours than on that of the strongly poisoned catalyst used for 12 hours without regeneration. As a result of the presence of an excess of oxygen, the temperatures in thermogram 2 (Fig. 4) were shifted to the lower range (from 302 to 255°). The presence of two constituents is seen especially clearly in this thermogram.

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* The analyses were carried out in the microanalytical laboratory of the Institute of Organic Chemistry of the Academy of Sciences of the USSR.

TABLE 1

Reaction conducted	Temperature		Analyses of poisoned catalysts			
	start of effect	maxima	% C	% H	atomic ratio H : C	wt. loss on calcination (%)
Dehydrogenation and dehydration of n-propyl alcohol	316°	382°	2.43	0.57	2.81	8.73
Conversion of xylene with steam	364	436 и 496	1.01	0.58	6.89	13.28

TABLE 2

Temperature of poisoning	Period of use without regeneration (in hours)	Temperature			Analyses			
		start of effect	1st maximum	2nd maximum	% C	% H	ratio H : C	wt. loss on calcination (%)
420°	2	240°	285°	318° (inflect)	1.57	0.31	2.37	2.60
420	6	239	283	340	—	—	—	4.67
350 — 420	12	302	370	475	7.19	0.39	0.66	8.72

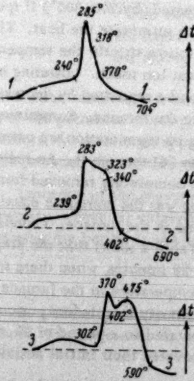

Fig. 3. Thermograms of chromium catalyst used for different periods of time in the decomposition of isopropyl alcohol (without regeneration):
1) 2 hours; 2) 6 hours; 3) 12 hours.

Curve 3 in Figure 4 corresponds to the thermogram of the last, most highly poisoned catalyst, which we recorded in vacuo while continuously pumping out the gases evolved. As was to be expected, the exothermic effects of combustion of the carbonaceous deposits were not observed in it (oxygen was absent), and instead there appeared here two high-temperature endothermic effects, which were explained by pyrolytic decomposition of the coating under investigation.

This thermogram shows that not only the temperatures of combustion but also the temperatures of pyrolytic decomposition in vacuo of the two constituents of the carbonaceous deposits differ from one another. A hypothesis concerning the possibility of stepwise combustion of the coating under investigation, first on the surface and then in the pores of the catalyst, failed because measurements made by A. E. Agronomov of the surface of the catalyst used showed that it was not porous; its surface was 135 m^2/g. An investigation of the poisoning of porous chromium catalysts will be further carried out by us.

Effect of temperature of poisoning of catalyst on the character of the carbonaceous deposits. In Figure 5 are presented the thermograms for a catalyst poisoned by us under exactly the same conditions with the same amount of starting material in the decomposition of isopropyl alcohol. Only the reaction temperature was changed.

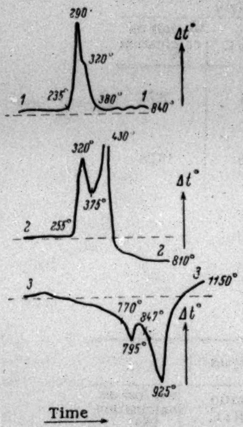

Fig. 4. Thermograms of poisoned chromium catalyst:
1) recorded in current of air for sample used 2 hours; 2) same for sample used 12 hours; 3) recorded in vacuo for sample used 12 hours.

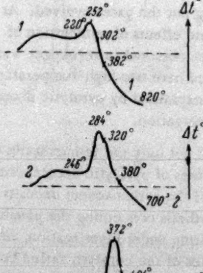

Fig. 5. Thermograms of chromium catalyst: 1) poisoned at 350°; 2) poisoned at 450°; 3) poisoned at 550°.

From the thermograms given it can be seen that an increase in the reaction temperature raises the starting temperature of the exothermic effect of combustion of the carbonaceous deposits and increases the area bounded by the curve. The latter circumstance is explained by an increase in the coating deposited.

Table 3 gives a comparison of the starting and maximum temperatures of the effects, the elementary analyses of the carbonaceous deposits, and the loss in weight of the samples on calcination.

In all three of the thermograms examined, after the maximum a small inflection in the course of the curve is observed, which may correspond to the combustion of a small amount of admixed second constituent; hence it is necessary to use a regeneration temperature not lower than this inflection point.

Investigation of the activity of regenerated catalysts. Besides the recording ot the thermograms of the poisoned catalysts, we carried out several experiments to investigate the activity of chromium oxide catalysts regenerated under different conditions. The temperature of the sample was observed by means of a platinum – rhodium thermocouple placed in the center of it. The activity of the different regenerated catalysts was checked in the dehydrogenation of cyclohexane, in which the poisoning itself was carried out. The data from these experiments is presented in Table 4.

Though the temperature at which exothermic effect of combustion of the coating starts does not depend on the size of the sample, the maximum and the end of this process depend wholly on its size. The amount of catalyst used for regeneration considerably exceeded the amount of the sample that we took for the recording of the thermograms (0.1-0.2 g); consequently, the temperature of the preparation during combustion of the carbonaceous deposits in the regeneration process might be very considerably increased (by 200-300°) if special precautionary measures were not taken to eliminate the heat. Thus, during regeneration it was necessary to follow strictly the temperature of the sample and not allow it to overheat too much. Lowering of the temperature in the catalyst layer can be regulated by decreasing the rate of supply of oxygen of the air to the furnace. Sometimes, to avoid overheating of the catalyst during its regeneration we passed a mixture of nitrogen with 2-5% of oxygen [6] through it. An indication that the carbonaceous coating had been completely removed from the surface of the preparation by combustion was the complete equalization of the temperature within the sample and in the furnace. Comparison of the data in the last two columns of Table 4 shows that the preparations regenerated in a total time of 20-25 minutes, when there still was not complete equalization of the temperature in the furnace and within the catalyst layer, had a lower activity than before poisoning. These same catalyst preparations regenerated in a period of 90 minutes at the same temperatures fully recovered their initial activity.

Previous recording of the thermogram of the poisoned catalyst gives the temperature of combustion of the carbonaceous deposits, below which it is impossible to regenerate the catalyst. The thermogram also shows the presence or absence of the second, very undesirable constituent of the carbonaceous coating, which requires a higher

TABLE 3

Temperature of poisoning	Temperature			Analyses			
	start of effect	maximum	inflection	% C	% H	atomic ratio H : C	wt. loss on calcination (%)
350°	220°	252°	302°	—	—	—	2.89
450	246	284	320	1.93	0.38	2.36	6.04
550	308	372	404	6.82	0.39	0.69	12.58

TABLE 4

Regeneration conditions			Reaction temperature	Rate of dehydrogenation (in ml/min) (STP)	
temperature		duration (in minutes)		before poisoning	after regeneration
in furnace	maximum in catalyst layer*				
392°	460°	90	440°	31.04	30.97
392	510	20	440	31.04	12.60
392	484	90	440	31.04	31.01
380	434	90	440	20.34	20.28
426	502	20	520	102.60	83.30
420	462	25	460	18.44	7.89
420	467	85	460	18.44	18.41
452	514	60	472	78.20	65.18
452	490	90	472	78.20	78.21
325	350	25	472	78.20	38.93
300	382	40	520	101.01	89.90
500	680	90	520	101.01	86.83
524	760	90	520	101.01	19.71

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* The variations in the maximum temperatures within the catalyst layer are explained by the difference in the rate of delivery of the current of air during regeneration.

regeneration temperature, and likewise indicates the character of the drop in the exothermic effect of combustion of the poisonous coating, which illustrates the necessity for a longer period of regeneration. Therefore, for a rational approach to the regeneration of the catalyst it is very desirable to have a thermogram of the poisoned preparation under the given conditions.

Lowering of the regeneration temperature of the catalyst is very desirable in general, and in industry, where all catalytic processes are carried out on a large scale, this may have great significance, increasing the period of use and improving the action of the catalyst.

SUMMARY

1. Poisoning of chromium catalysts by carbonaceous deposits has been investigated by the thermographic method. The difference in character of these deposits, depending on the reaction carried out, has been confirmed.

2. It has been established that in some instances the carbonaceous coating has two constituents, one of which has a higher combustion temperature than the other. Raising the reaction temperature and increasing the period of use of the catalyst without regeneration increase the amount of this second, very undesirable constituent.

3. The presence of the two indicated constituents of the carbonaceous coating on chromium catalysts poisoned in the decomposition of isopropyl alcohol has been confirmed by recording the thermograms of the

poisoned catalysts in vacuo while continually removing the gases evolved. Instead of the bifurcated exothermic effect of combustion of the carbonaceous deposits, two clearly shown endothermic effects of pyrolytic decomposition of the two constituents of the deposits were observed in the vacuum thermograms.

4. Use of differential thermal analysis for the investigation of the character of the combustion of the carbonaceous deposits and the determination of the combustion temperature of these deposits have made it possible to approach rationally the problem of the regeneration of catalysts, to control their combustion, and in some instances also to lower the temperature of this process.

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PHYSICOCHEMICAL ANALYSIS OF THE SYSTEM FORMIC ACID – DIMETHYLFORMAMIDE

DENSITY, VISCOSITY, AND ELECTRICAL CONDUCTIVITY IN THE SYSTEM FORMIC ACID – DIMETHYLFORMAMIDE

M. D. Korol'kova and B. K. Kricheviov

It is known that amides are able to form complex compounds mainly with organic [1-4] and inorganic [5] acids. In this connection the physicochemical analysis of the binary system formed by formic acid and its simplest dialkyl-substituted amide, dimethylformamide, is of theoretical and practical interest. With regard to this system there are in the literature only contradictory indications that its components form azeotropes with a maximum boiling point [6, 7]. More complete data on the nature of the reaction between formic acid and dimethylformamide are lacking in the literature.

In the present work we have set up the problem of investigating some of the physicochemical properties of the system formed by formic acid and dimethylformamide, in particular the density, viscosity, and electrical conductivity, and of showing to what extent the results obtained by us agree with the contemporary idea of the properties of such systems.

EXPERIMENTAL

Formic acid was purified by repeated rectification on a laboratory column under conditions that excluded contact with the moisture of the air. The purified acid boiled at 100.38° (757.4 mm) d^{20}_4 1.2201, $n^{20}D$ 1.3710. Dimethylformamide was prepared from pure formic acid and dimethylamine. The product was purified by two fractional distillations on the laboratory column, after which it had the following physicochemical constants: b.p. 153° (760 mm), d^{20}_4 0.9484, $n^{25}D$ 1.4283. The solutions for the physicochemical investigations were prepared by weight. Since mixing of the components was accompanied by a considerable heat effect, the preparation of the solutions was carried out with cooling. Measurements were made at 20, 25, 80 and 100°. The temperature in the thermostat was maintained with an accuracy of 0.1°. The viscosity was determined in an Ostwald viscosimeter, and the density was determined with a pycnometer. The electrical conductivity was measured by the Kohlrausch method in closed vessels with a platinum electrode.

Experimental Data and Discussion of Results

The values obtained for the densities and the calculated molar volumes, the values of the viscosity and the specific electrical conductivity of the formic acid and dimethylformamide solutions at 20, 25, 80 and 100° are presented in Tables 1-3 and in Figure 1.

As can be seen from Figure 1, the density isotherms for the indicated system are curves that are slightly convex toward the axis of composition.

The viscosity isotherm at 20° has a clear maximum in the formic acid vicinity and, moreover, it is characterized by the presence of a point of inflection at ~50 mole% of formic acid. With an increase in temperature the maximum in the curve becomes less distinct and the point of inflection is shifted in the direction of dimethylformamide. The electrical conductivity isotherms at all temperatures have a maximum in the

TABLE 1

Density and Molecular Volumes in the System Formic Acid – Dimethylformamide

Density molecular volume	Formic acid content (in mole %)								
	0	10	20	30	35	40	45	50	55
d_4^{20}	0.9484	0.9628	0.9783	0.9963	1.0047	1.0161	1.0238	1.0385	1.0506
v_{20}	76.97	73.015	69.099	65.14	63.52	61.21	59.43	57.29	55.34
d_4^{80}	0.8920	0.9059	0.9201	0.9397	0.9485	0.9580	0.9681	0.9803	0.9883
v_{80}	81.83	77.50	73.47	69.05	67.08	64.93	62.85	60.59	58.77
d_4^{100}	0.8749	0.8881	0.9022	0.9189	0.9274	0.9371	0.9454	0.9598	0.9679
v_{100}	83.43	79.15	74.92	70.65	68.52	66.37	64.36	61.99	60.07

TABLE 2

Viscosity in the System Formic Acid – Dimethylformamide

η (in cp) at temperature	Formic acid content (in mole %)								
	0	10	20	30	35	40	45	50	55
20°	0.8428	0.9502	1.0502	1.1954	1.2574	1.3543	1.4533	1.5480	1.6380
80	0.4318	0.4530	0.4913	0.5480	0.5777	0.5773	0.5982	0.6209	0.6415
100	0.3749	0.3618	0.3914	0.4206	0.4427	0.4529	0.4698	0.4815	0.4964

TABLE 3

Electrical Conductivity in the System Formic Acid – Dimethylformamide

$\kappa \cdot 10^4$ at temperature	Formic acid content (in mole %)								
	0	10	20	30	35	40	45	50	55
20°	0.01364	2.02	2.77	3.40	3.64	3.95	4.64	5.04	7.03
25	0.04334	2.14	2.93	3.68	3.89	4.32	5.06	6.54	8.81
80	0.05071	3.48	4.75	6.48	7.50	9.06	10.99	14.11	18.13
100	0.07038	4.29	6.09	8.36	10.36	12.76	15.38	19.75	25.16

TABLE 4

Temperature Coefficients of Electrical Conductivity (β), Viscosity (γ), and Electrical Conductivity Adduced in the System Formic Acid – Dimethylformamide

	Formic acid content (in mole %)							
	0	10	20	30	35	40	45	50
$\beta \cdot 10^3$ (20 – 80°)	2.51	8.85	8.77	10.36	11.54	13.08	13.53	14.04
$\beta \cdot 10^3$ (20 – 100°)	5.85	9.02	9.38	10.55	11.98	13.18	13.43	14.82
$\gamma \cdot 10^3$ (20 – 80°)	10.75	12.72	12.12	12.38	12.35	13.41	13.89	14.24
$\gamma \cdot 10^3$ (20 – 100°)	9.61	11.20	11.42	11.94	11.96	12.46	12.77	13.00
$\varkappa\eta \cdot 10^4$ (20°)	0.03678	1.92	2.92	4.07	4.58	5.36	6.74	7.8

	60	65	70	75	80	85	90	95	100
	1.0645	1.0773	1.0948	1.1107	1.1278	1.1478	1.1696	1.1947	1.2201
	53.35	51.48	49.41	47.49	45.55	43.60	41.63	39.63	37.70
	1.0061	1.0161	1.0294	1.0472	1.0620	1.0807	1.1016	1.1252	1.1461
	56.55	54.57	52.55	50.37	48.39	46.31	44.20	42.08	40.13
	0.9827	0.9971	1.0079	1.0236	1.0399	1.0583	1.0794	1.0018	1.1158
	57.78	55.59	53.67	51.53	49.42	47.29	45.11	42.97	41.22

	60	65	70	75	80	85	90	95	100
	1.7353	1.8230	1.8639	1.9154	1.9509	1.9475	1.9215	1.8769	1.7761
	0.6891	0.6787	0.6823	0.6954	0.6989	0.6897	0.7007	0.6849	0.6354
	0.5322	0.5502	0.5234	0.5249	0.5196	0.5191	0.5139	0.4975	0.4807

	60	65	70	75	80	85	90	95	100
	11.50	16.12	22.88	30.39	38.70	46.23	49.57	44.08	5.78
	12.78	17.91	24.68	32.74	41.63	49.72	53.14	47.33	6.29
	25.10	33.38	43.53	56.01	69.06	80.39	84.47	74.25	9.70
	32.80	43.37	52.08	65.45	79.50	89.52	92.71	80.62	

	55	60	65	70	75	80	85	90	95	100
	14.71	12.38	11.62	10.36	9.88	9.39	8.99	8.68	8.5	
	14.10	12.02	11.46	9.74	9.15	8.63	7.98	7.58	7.28	
	14.57	14.38	15.24	15.47	15.57	15.69	15.89	15.52	15.51	15.76
	13.37	13.25	13.42	14.02	14.25	14.52	14.48	14.51	14.51	14.35
	11.5	19.96	29.39	42.65	58.21	75.5	90.03	95.25	82.75	10.27

region near formic acid. In order to establish more exactly the relationship of the electrical conductivity to the composition, we calculated the relative temperature coefficients of electrical conductivity (β).

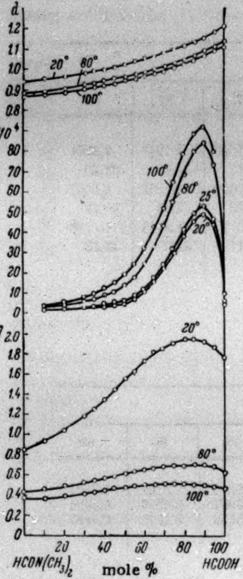


Fig. 1. Density (d), specific electrical conductivity ($\varkappa$) and viscosity (η) in the system formic acid – dimethylformamide.

$$\beta = \frac{1}{\frac{\varkappa_1 + \varkappa_2}{2}} \cdot \frac{\varkappa_2 - \varkappa_1}{t_2 - t_1}$$

The temperature coefficients of viscosity (γ) were similarly calculated. The appropriate data are shown in Table 4 and Fig. 2. Here also are shown the values of the adduced electrical conductivity ($\varkappa\eta$) and the isotherms of molar volume (v).

The viscosity isotherms, which are characterized, as shown above, by a point of inflection, are indicative of a chemical reaction. As noted by N. S. Kurnakov, the presence of such S-like isotherms is characteristic of systems with a definite reaction [8]. The presence of a maximum in the viscosity isotherm at 20° in the region of high formic acid content can be explained by the further reaction of the compound formed with the formic acid. The complex originating as a result of this breaks down at a higher temperature. Hence, this maximum is very weak in the viscosity isotherms at 80 and 100°.

The isotherms of specific electrical conductivity have a maximum in the vicinity of pure formic acid. This maximum cannot be explained by the change in viscosity alone, since the electrical conductivity isotherm adjusted for the viscosity at 20° does not essentially change in appearance (Fig. 2). It also does not indicate the composition of the chemical compound formed. The composition of the compound formed is indicated by the break in the electrical conductivity isotherm at 20°, which corresponds to a 1:1 compound, and the maximum in the relative temperature coefficient curves also indicates its composition. The presence of the maximum in the electrical conductivity isotherm in the formic acid vicinity apparently should be explained by electrolytic dissociation of the compound formed.

Thus, the compound of 1:1 composition in the system formic acid – dimethylformamide appears in the viscosity and electrical conductivity isotherms and also in the curves of relative temperature coefficient versus composition. We can represent the reaction of dimethylformamide with formic acid in the following way, starting from the presence of a hydrogen bond and taking into consideration the electron-donor properties of the nitrogen of dimethylformamide.

TABLE 5

Molecular Weights of Mixtures of Formic Acid and Dimethylformamide

Composition of dimethylformamide – formic acid mixture	Molecular weight			
	average for simple mixture (calculated)	theoretical for 1:1 compound (calculated)	average for 1:1 mixture of dimethylformamide with compound (calculated)	cryoscopically determined
1:1	59.5	119	–	111.85
2:1	64.0	–	96.0	98.90

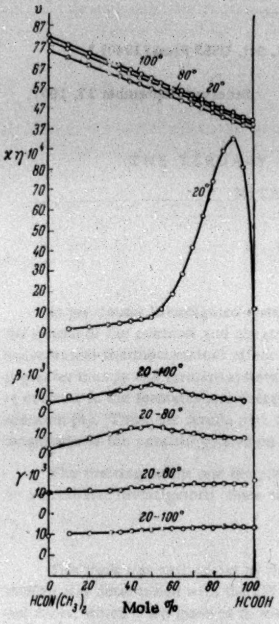
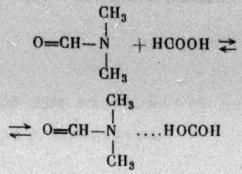


Fig. 2. Molecular volume (v), adduced electrical conductivity (x η), temperature coefficient of electrical conductivity (β), and temperature coefficient of viscosity (γ) in the system formic acid – dimethylformamide.



$$\mathrm{O{=}CH{-}\underset{CH_3}{\overset{CH_3}{N}} + HCOOH \rightleftarrows}$$

$$\mathrm{\rightleftarrows O{=}CH{-}\underset{CH_3}{\overset{CH_3}{N}} \;\ldots\ldots HOCOH}$$

Special studies have shown that when a solution of formic acid in dimethylformamide is boiled, the acid breaks down into water and carbon monoxide. In view of this, it was not possible to study the liquid-vapor equilibrium at constant pressure (760 mm) for this system.

The presence of a compound of dimethylformamide with formic acid in 1:1 ratio was confirmed by cryoscopic investigation of mixtures of dimethylformamide with formic acid. Benzene was used as the solvent. The results of these determinations are given in Table 5.

As follows from the data on Table 5, the molecular weights of the 1:1 and 1:2 mixtures determined by the cryoscopic method are close to the molecular weights calculated theoretically for the 1:1 compound and its mixture with dimethylformamide, and differ sharply from those calculated for a simple mixture of these materials. This again confirms the existence of a chemical compound of dimethylformamide and formic acid in the 1:1 ratio.

SUMMARY

1. The density, viscosity, and specific electrical conductivity in the system dimethylformamide – formic acid has been investigated at 20, 25, 80 and 100°.

2. The isotherms of viscosity and electrical conductivity, the curves for the temperature coefficients of electrical conductivity, and cryoscopic measurements of molecular weight show the presence in the system of the compound $\mathrm{HCOOH \cdot HCON(CH_3)_2}$.

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THE TERNARY MUTUAL SYSTEM OF THE PROPIONATES AND NITRATES OF SODIUM AND POTASSIUM

O. I. Dmitrevskaia and N. M. Sokolov

In previously investigated systems of the formates and nitrates of sodium and potassium [1] and also in the system of the acetates and nitrates of these metals [2, 3] the direction of the reaction conforms with the conventional thermochemical effect of the reaction, whereby the degree of irreversibility in the acetate system is greater than in the formate system. The system considered here is the next link in this series. Unfortunately, in contrast to the formates and acetates the propionates have been little studied and their heats of formation are unknown [4]. Thus, the results with the present system can be compared only in the light of the effect of the magnitude of the paraffin portion on the process in the fused materials.

The melting points and the presence of polymorphic transformations have been determined for the nitrates by a number of investigators; these same data for the propionates were obtained for the first time by one of us.

EXPERIMENTAL

The work was carried out by the visual polytherm method. The temperature of appearance of the first crystals was determined with the aid of a nichrome-constantin thermocouple. The salts were melted in glass test tubes, which were inserted in wider tubes to ensure uniform heating. For vigorous agitation, glass fiber stirrers were used. The freezing points of the following substances were used as "bench marks", benzoic acid (121.5°), mannitol (167°), succinic acid (187°), silver nitrate (208°), tin (231.5°), potassium nitrate (337°), potassium bichromate (396°), and the boiling point of water (100°).

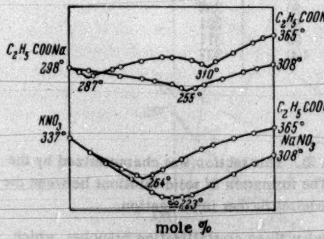


Fig. 1. Binary system.

Commercial, chemically pure preparations of sodium and potassium nitrates, which were recrystallized, were used for the work. To prepare the propionates, propionic acid was added to solutions of the chemically pure bicarbonates, first to neutrality and then in small excess. Commercial propionic acid was purified by distillation. The dry salts C_2H_5COONa and C_2H_5COOK that were obtained after evaporation were purified by recrystallization from butanol. The melting points of the starting salts were: KNO_3 337°, $NaNO_3$ 308°, C_2H_5COOK 365°, C_2H_5COONa 298°. Transformations in the solid state were observed for all the salts: KNO_3 had transformations at 124° and 316° [5, 6]; $NaNO_3$ at 275° [6-8]; for C_2H_5COONa polymorphic transformations in the solid state observed at 77, 195, 217 and 287° [9]; and for C_2H_5COOK at 68° [9].

All compositions are given in mole percent.

Binary Systems

1. The system $NaNO_3-KNO_3$ has been studied by many authors [10-14]. We used the data from [14]. The system presents a continuous series of solid solutions with a minimum at m.p. 223° and 50% KNO_3 (Fig. 1).

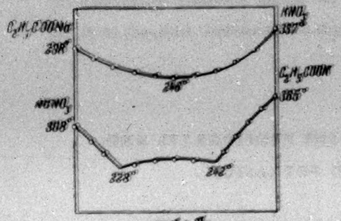


Fig. 2. Diagonal sections.

2. The system $C_2H_5COOK-KNO_3$ was investigated for the first time. Two branches of the curve intersect at 264° and 65% KNO_3 (Table 1, Fig. 1).

3. The system $C_2H_5COONa-C_2H_5COOK$ has been described previously [15]. The branches of the melting curve intersect in two points at 287° and 8% C_2H_5COOK and at 310° and 66% C_2H_5COOK. In this system a compound is formed, with the probable composition $2C_2H_5COONa \cdot 3C_2H_5COOK$ (Table 1, Fig. 1).

4. The system $C_2H_5COONa-NaNO_3$, which has been studied previously [16], presents a eutectic system; two branches of the melting curve intersect at 255° and 56.5% $NaNO_3$ (Table 1, Fig. 1).

TABLE 1

Binary Systems

$C_2H_5COONa-C_2H_5COOK$		$C_2H_5COONa-NaNO_3$		$C_2H_5COOK-KNO_3$	
mole % C_2H_5COOK	temperature	mole % $NaNO_3$	temperature	mole % KNO_3	temperature
0	298°	0	298°	0	365°
5	292	5	294	5	360
8	287	10	291	10	354
10	294	15	287	15	348
15	303	20	284	20	341
20	307	25	282	25	335
30	310	30	280	30	328
35	315	35	276	35	321
40	316	40	273	40	310
45	317	45	269	45	300
50	317	50	264	50	292
55	318	55	258	55	281
60	319	56.5	255	60	272
65	314	60	261	62.5	267
66	310	65	270	65	264
70	316	75	280	67.5	268
75	322	85	290	70	274
85	340	95	301	75	282
90	351	100	308	80	292
95	358			85	301
100	365			90	311
				100	337

Diagonal Sections

1. Stable diagonal section $C_2H_5COONa-KNO_3$ (Table 2, Fig. 2). This section was characterized by the presence of solid solutions and a minimum melting point of 246°. The formation of solid solutions between the stable pair of salts is one of a few cases, the explanation of which requires further investigation.

2. Unstable diagonal $C_2H_5COOK-NaNO_3$. The melting curve has three crystallization branches, which intersect in two points: at 242° and 30% $NaNO_3$ and at 228° and 77.5% (Table 2, Fig. 2).

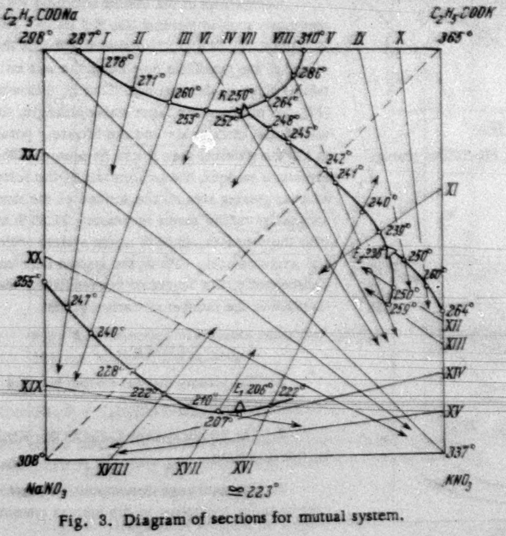
Melting Diagram of Mutual System

From the results of the investigation of the binary systems, the diagonals, and the 21 interior sections (Fig. 3-6) a projection was constructed of the curves of joint crystallization on the surface of the polytherm of the binary system $NaNO_3-KNO_3$ (Fig. 7). On the basis of these data the position of the triple points was determined and the fields of crystallization of the salts, complexes, and solid solutions were delimited. The

TABLE 2

Diagonal Sections

$C_2H_5COONa-KNO_3$ (stable)				$C_2H_5COOK-NaNO_3$ (unstable)			
mole % KNO_3	temperature	mole % KNO_3	temperature	mole % $NaNO_3$	temperature	mole % $NaNO_3$	temperature
0	298°	55	247°	0	365°	75	233°
5	290	57.5	248	5	351	77.5	228
10	283	60	250	10	332	80	237
15	276	62.5	251	15	313	82.5	248
17.5	273	65	253	20	292	85	256
20	270	67.5	256	22.5	280	90	274
22.5	267	70	258	25	268	95	291
25	264	72.5	261	27.5	253	100	308
27.5	262	75	265	30	242		
30	258	77.5	268	32.5	243		
32.5	256	80	273	35	244		
35	254	82.5	278	40	245		
37.5	251	85	284	45	246		
40	249	87.5	291	50	246		
42.5	247.5	90	298	55	245		
45	246.5	95	315	60	244		
47.5	246	100	337	65	242		
49	245.5			70	238		
50	246			72.5	236		
52.5	246.5						



C_2H_5COONa
C_2H_5COOK
298°
287°
I
II
III
VI
IV
VII
VIII
310°
V
IX
X
365°
278°
271°
260°
K 250°
286°
264°
253°
252°
248°
245°
242°
241°
240°
239°
E_2 236°
250°
260°
250°
259°
264°
XXI
XX
XI
XII
XIII
XIV
XV
255°
247°
240°
228°
222°
210°
E_1 206°
222°
207°
XIX
308°
337°
XVIII
XVII
XVI
$NaNO_3$
KNO_3
≅223°

Fig. 3. Diagram of sections for mutual system.

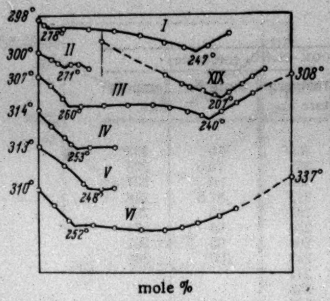


Fig. 4. Interior sections I-VI, XIX of mutual system.

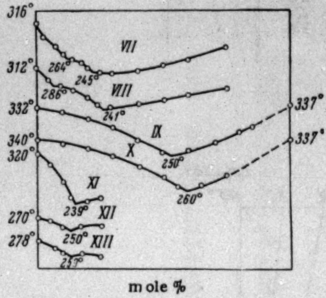


Fig. 5. Interior sections VII-XIII of mutual system.

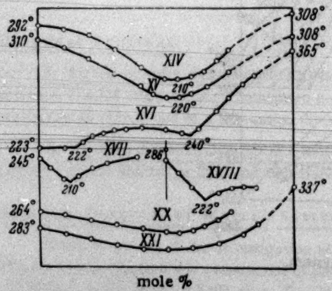


Fig. 6. Interior sections XIV-XVIII, XX-XXI of mutual system.

projection of the diagram of the liquidus of the ternary mutual system on the composition square with isotherms drawn through 20° is given in Figure 8.

The surface of the liquidus of the mutual system consists of the field of compound $2C_2H_5COONa \cdot 3C_2H_5COOK$, the field of C_2H_5COOK, and the fields of the solid solutions. The solid solutions Na, K ‖ NO_3 have a tendency to break down only at a temperature below 206°. The congruently melting compound $2C_2H_5COONa \cdot 3C_2H_5COOK$, which is formed in the binary system $C_2H_5COONa - C_2H_5COOK$, decomposes in the mutual system and terminates its existence at the point R. The ternary mutual system is divided by the stable diagonal section $C_2H_5COONa - KNO_3$ into two phase triangles.

1. $C_2H_5COONa - KNO_3 - NaNO_3$ with the ternary eutectic point E_1 at 206° and 11.5% C_2H_5COONa, 47.5% KNO_3, 41% $NaNO_3$.

2. $C_2H_5COONa - KNO_3 - C_2H_5COOK$, in which there is a ternary eutectic point E_2 at 238° and 13.5% C_2H_5COONa, 37% KNO_3, 49.5% C_2H_5COOK and a transition point R at 250° and 40% C_2H_5COONa, 15.5% KNO_3, 35.5% C_2H_5COOK.

The system investigated, in spite of the presence of complex formation on the side $C_2H_5COONa - C_2H_5COOK$, is related to the irreversible-mutual systems with a stable diagonal.

Comparison of the results obtained with the data of the previously studied systems Na, K ‖ HCOO, NO_3 [1] and Na, K ‖ CH_3COO, NO_3 [2, 3] makes it possible to deduce the effect of the paraffinic portion of the salt on the processes taking place in the fusions. Thus if, following A. I. Palkin [17], we examine the same stable triangle, that of the sodium salt of the fatty acid – sodium nitrate – potassium nitrate, in all the systems, then it can be seen that the field of the exchange product, the sodium salt of the fatty acid, occupies an ever greater area on the surface of the liquidus as the number of carbon atoms increases: 31.37% in the system with the formates, 48.27% in the system with the acetates, and approximately 61% in the system here under investigation. Consequently, the degree of irreversibility increases with an increase in the number of carbon atoms.

SUMMARY

1. The ternary mutual system Na, K ‖ C_2H_5COO, NO_3 has been studied.

2. The binary system $C_2H_5COOK - KNO_3$ has been studied for the first time.

3. The exchange decomposition reaction predominates over complex formation in the mutual system.

4. The formation of solid solutions on the stable diagonal $C_2H_5COONa - KNO_3$ has been established, which is contrary to the theory of isomorphism and therefore requires further investigation.

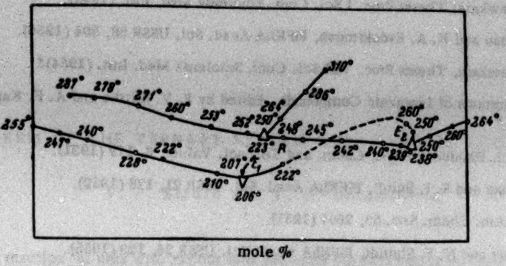


Fig. 7. Projection of joint crystallization curves of mutual system Na, K ‖ C_2H_5COO, NO_3 on the side $NaNO_3-KNO_3$.

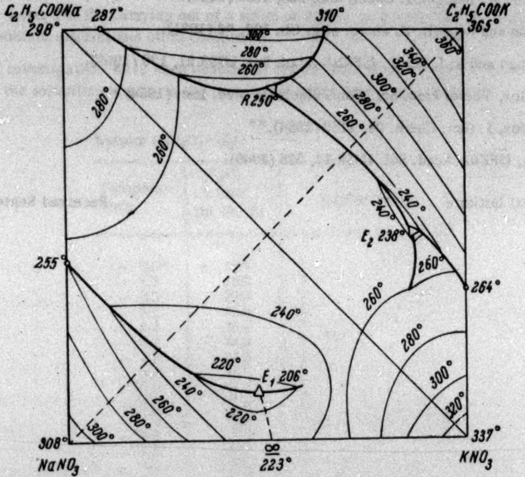

C2H5COONa
298°
287°
310°
C2H5COOK
365°
360°
340°
320°
300°
280°
260°
R 250°
280°
260°
300°
280°
260°
240°
240°
E2 238°
260°
264°
255°
240°
260°
280°
300°
320°
220°
E1 206°
240°
260°
280°
300°
220°
308°
NaNO3
223°
KNO3
337°

Fig. 8. Projection of liquidus surface of system Na, K ‖ C_2H_5COO, NO_3 on composition square.

5. The system Na, K ‖ C_2H_5COO, NO_3 has been classified as irreversible – mutual with a stable diagonal.

6. The effect of the number of carbon atoms on the degree of irreversibility of the exchange reaction between the potassium salt of the fatty acid and sodium nitrate has been ascertained.

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POLYTHERM OF THE TERNARY SYSTEM UREA – CITRIC ACID – WATER

V. P. Blidin and T. G. Golovanova

A study of the reaction of urea with various salts and acids has both theoretical and practical significance in connection with the preparation of mixed fertilizers. Urea is the very best concentrated nitrogen fertilizer. Citric acid is present in small amounts in soils, and citric acid salts play an important physicochemical role in the stabilization of colloidal particles of mineral and organic origin in the soils. They also improve the absorbing capacity of the soils and provide some degree of permanence for very valuable fertilizers.

In this connection we established as our goal the investigation of the polytherm of the ternary system urea –citric acid–water and the carrying out of a series of studies on the reaction of urea with potassium, calcium, and ammonium citrates and other compounds.

A number of investigations have been devoted to the question of the reaction of urea with other materials [1-6]. We studied the solubility of urea in the presence of citric acid for the first time.

System $C_6H_8O_7-H_2O$

Temperature	$C_6H_8O_7$ content (in wt. %)	Bottom Phase
— 0.9°	10.0	Ice
— 1.7	15.0	
— 2.5	20.0	
— 3.2	25.0	
— 4.3	30.0	
— 5.8	34.0	
— 7.2	38.0	
— 9.8	42.5	
—10.6	44.0	
—12.4	47.6	
—13.6	48.9	Ice + $C_6H_8O_7 \cdot H_2O$
—10.5	50.6	$C_6H_8O_7 \cdot H_2O$
— 5.5	51.9	
— 3.0	52.8	
+ 5.0	54.5	
+15.0	57.5	
+20.0	59.0	

According to data in the literature [2], the cryohydric point of the system $CO(NH_2)_2-H_2O$ lies at $-11.0°$. This corresponds to the composition 32.9% urea and 67.1% water. In the urea branch of the crystallization curve there are two discontinuities – the first at $+1.1°$, corresponding to 40.7% urea, and the second at 24.4°, corresponding to 54.5% urea. Thus, α-, β-, and γ-modifications of urea exist.

The cryohydric point of the system $C_6H_8O_7-H_2O$ (Table, Fig. 1), according to our data, corresponds to $-13.6°$ and 48.9% $C_6H_8O_7$.

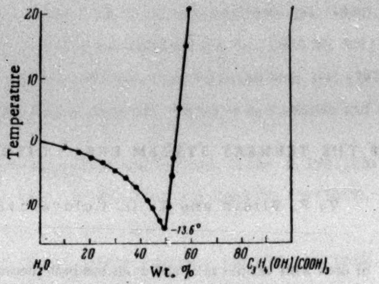


Fig. 1. Polytherm of $C_3H_4(OH)(COOH)_3-H_2O$.

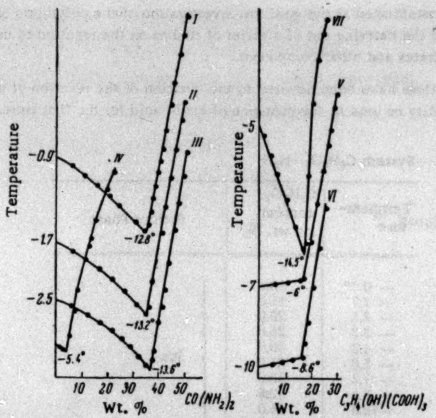


Fig. 2. Sections of ternary system; explanation in the text.

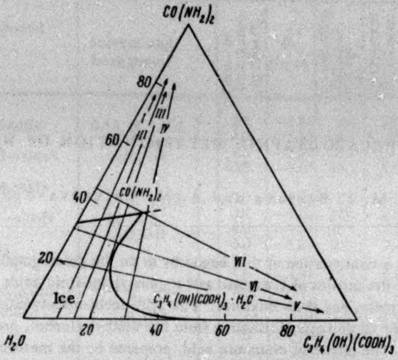
EXPERIMENTAL

Chemical pure compounds were used for the work. The investigation was carried out by the visual polytherm method, which consists in determining the disappearance and appearance of the first crystals at certain temperatures fixed by observation. The accuracy of the observations was ± 0.1°.

Seven interior sections were studied to obtain the diagram of the ternary system. These sections are shown in Fig. 2. The directions of the sections are shown in Fig. 3.

On the basis of the data from the sections a diagram of the polytherm was constructed (Fig. 3). In the diagram we see the field of crystallization of ice tapering in the direction of $C_6H_8O_7$, and the unbounded fields of urea and citric acid.

In the system there is one triple point corresponding to 35.8% $CO(NH_2)_2$, 16.5% $C_6H_8O_7$, and 47.4% H_2O. The melting point of the triple eutectic is $-14.5°$.



$CO(NH_2)_2$
80
60
40
20
I
II
III
IV
$CO(NH_2)_2$
VII
VI
V
Ice
$C_3H_4(OH)(COOH)_3 \cdot H_2O$
H_2O
20
40
60
80
$C_3H_4(OH)(COOH)_3$

Fig. 3. Diagram of polytherm.

The α-, β-, and γ-modifications of urea were not observed by us in the presence of citric acid.

SUMMARY

1. The system urea—citric acid—water has been investigated by the visual polytherm method. The absence of chemical compounds and solid solutions has been established.

2. The ternary eutectic point has been determined, corresponding to the composition 35.8 % $CO(NH_2)_2$, 16.5% $C_6H_8O_7$, and 47.7% H_2O.

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POLAROGRAPHIC DETERMINATION OF NITRILES

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The present work is a continuation of that begun by us on the polarography of nitriles [1]. The objects of the investigations were the nitriles of cinnamic and α-phenylcinnamic acids, the dinitrile of fumaric acid * and 2,2'-azobisisobutyronitrile, and their mixtures. The 2,2'-azobisisobutyronitrile was a commercial product with a stabilizer added. By triple recrystallization from hot methyl alcohol, previously purified, a product was obtained with m.p. 101°. The nitrile of cinnamic acid, prepared by the method described in the literature [2], had the m.p. 254-256° and $n^{20}D$ 1.5980. The nitrile of α-phenylcinnamic acid was synthesized by a method published in a collection of papers [3], m.p. 86-88°. The dinitrile of fumaric acid melted at 96°.

EXPERIMENTAL

Polarographing was carried out within concentration limits from 1 to 10 mM/liter on a M-7 polarograph with a mirror galvanometer having a sensitivity of 150 mm/μA. As the background electrolyte, 75 and 50% alcohol–water solutions of 0.14 N lithium chloride were used.

The measurements were mainly carried out with a 1/10 shunt. The capillary was cylindrical with a dropping period τ = 3 sec and mass of the mercury drop m = 1.91 mg/sec, $m^{2/3} \cdot \tau^{1/6} = 1.83$ mg$^{2/3}$·sec$^{-1/2}$ at a voltage of 2.1 v.

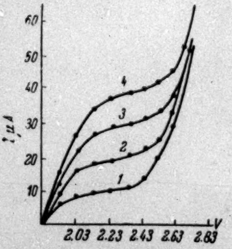

Fig. 1. Polarograms of nitrile of cinnamic acid (background LiCl in 75% C_2H_5OH): Concentration (in moles/liter): 1) $2.5 \cdot 10^{-3}$; 2) $5.0 \cdot 10^{-3}$; 3) $7.5 \cdot 10^{-3}$; 4) $10 \cdot 10^{-3}$.

The height of elevation of the bulb with the mercury provided for possible tangential movements [4].

It follows from an examination of the experimental data that the reduction of the nitriles of cinnamic and α-phenylcinnamic acids and 2,2'-azobisisobutyronitrile takes place in one stage, but the reduction of the dinitrile of fumaric acid proceeds in two stages.

It should be noted that only one wave was observed when we previously polarographed the dinitrile of fumaric acid, because a very dilute solution of the background electrolyte was used [1].

For the first stage of the reduction there is a corresponding wave with a half-wave potential $E_{1/2} = -1.30$ v, and for the second stage there is a wave with $E_{1/2} = -2.2$ v (Fig. 1 and 2).

Reduction of the nitrile of α-phenylcinnamic acid proceeds with more difficulty than that of the dinitrile of fumaric acid, and 2,2'-azobisisobutyronitrile, as indicated by the more negative value of the half-wave potential of this nitrile, namely, −1.94 v in 0.14 N solution of LiCl in 50% ethyl alcohol. The nitrile of cinnamic acid is reduced under still more severe conditions than the nitrile of α-phenylcinnamic acid. This follows from the fact that the half-wave potential of the nitrile of α-phenylcinnamic acid

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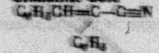
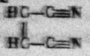
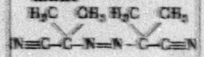
* The nitriles named were synthesized by A. Kh. Khomenko.

Expt. No.	Name of compound and formula	Solvent and background	Conc. of compound (in mM/l)	$E_{1/2}$* (in v)	i_d Limiting diffusion current (in μA)	I_d Constant of diffusion current	n Number of electrons per mole of compound
1	Nitrile of cinnamic acid $C_6H_5CH{=}CH{-}C{\equiv}N$	0.14 N LiCl in 75% C_2H_5OH	2.5	—1.90	9.8	2.14	0.48
			5.0	—1.93	19.0	2.08	
			7.5	—1.97	28.4	2.07	
			10.0	—1.97	70.2	2.14	
2	Nitrile of α-phenylcinnamic acid  $C_6H_5CH{=}C(C_6H_5){-}C{\equiv}N$	0.14 N LiCl in 75% C_2H_5OH	2.0	—1.83	7.9	2.17	0.52
			3.0	—1.85	12.0	2.18	
			4.0	—1.87	16.1	2.20	
			5.0	—1.88	20.9	2.22	
3	Nitrile of α-phenylcinnamic acid	0.14 N LiCl in 50% C_2H_5OH	1.0	—1.91	2.9	1.60	0.64
			2.0	—1.94	5.9	1.61	
			3.0	—1.96	8.7	1.60	
			4.50	—1.97	11.6	1.60	
			5.0	—1.98	14.5	1.60	
4	Dinitrile of fumaric acid  $HC{-}C{\equiv}N \parallel HC{-}C{\equiv}N$	0.14 N LiCl in 50% C_2H_5OH	2.0	—1.27	4.65	1.27	For 1st wave 0.32
				—2.10	6.20	1.69	
			3.0	—1.30	7.20	1.31	
				—2.16	9.20	1.68	
			4.0	—1.31	9.60	1.31	
				—2.19	12.30	1.68	
			5.0	—1.32	12.0	1.31	
				—2.22	15.30	1.67	For 2nd wave 0.38
			6.0	—1.3	14.55	1.31	
				—2.22	18.30	1.64	
5	2,2'-Azobisisobutyronitrile  $N{\equiv}C{-}C(CH_3)_2{-}N{=}N{-}C(CH_3)_2{-}C{\equiv}N$	0.14 N LiCl in 50% C_2H_5OH	1.0	—1.71	3.0	1.63	0.35
			2.0	—1.75	6.0	1.63	
			3.0	—1.78	9.1	1.63	
			4.0	—1.81	12.2	1.64	
			5.0	—1.85	15.3	1.64	
			6.0	—1.88	18.2	1.63	

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* The values of the half-wave potentials (relative to a saturated calomel electrode) are given without correction for it, as a result of which their magnitude increases with an increase in concentration. A correction was not made because there is not as yet the requisite clarity in the evaluation of the resistance of the working electrolyzer either in our data or that in the literature [5, 6].

in 75% ethyl alcohol is − 1.85 v, and the half-wave potential of the nitrile of cinnamic acid under the same conditions is − 1.95 v (Table).

In all instances the magnitude of the limiting diffusion current was proportional to the concentration of the nitrile, as indicated by the calibration line (Fig. 3).

From the wave equation based on the graph $\log \frac{i}{id - i}$ vs. (E) (Fig. 4), we find the number of electrons expended in the reduction of 1 mole of nitrile at the mercury drop. The fractional values obtained for n show the irreversibility of the reduction process occurring at the mercury drop.

When we polarographed mixtures of the nitrile of α-phenylcinnamic acid, the dinitrile of fumaric acid, and 2,2'-azobisisobutyronitrile, we obtained polarograms with diffusion waves corresponding to the reduction of each of the components (Fig. 5).

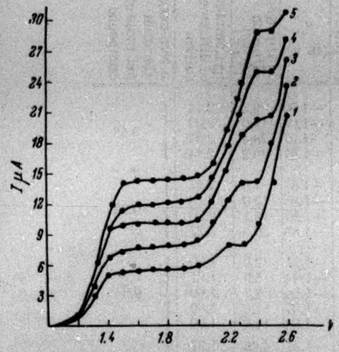

Fig. 2. Polarograms of dinitrile of fumaric acid (background LiCl in 50% C_2H_5OH): concentration (in moles/liter): 1) $1 \cdot 10^{-3}$; 2) $3 \cdot 10^{-3}$; 3) $4 \cdot 10^{-3}$; 5) $5 \cdot 10^{-3}$.*

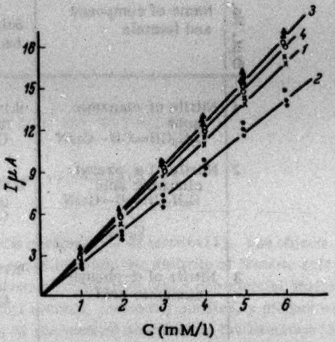

Fig. 3. Graduation lines: 1) nitrile of α-phenylcinnamic acid; 2) dinitrile of fumaric acid (1st wave); 3) same (2nd wave); 3) 2,2'-azobisisobutyronitrile (background LiCl in 50% C_2H_5OH).

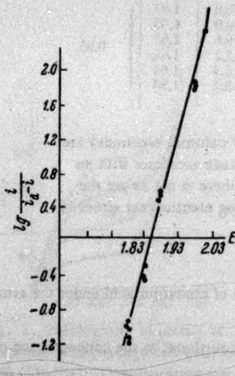

Fig. 4. Logarithmic line for nitrile of α-phenylcinnamic acid (background LiCl in 75% C_2H_5OH).

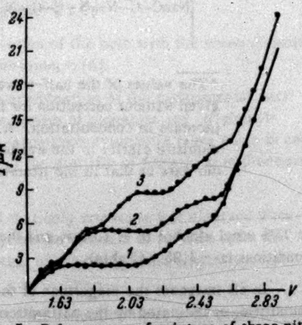

Fig. 5. Polarograms of mixture of three nitriles, concentration $1 \cdot 10^{-3}$ mole/liter (background LiCl in 50% C_2H_5OH): 1) dinitrile of fumaric acid; 2) azodinitrile of isobutyric acid; 3) nitrile of α-phenylcinnamic acid.

All of the polarographic properties inherent in each material individually retained their values in the main.

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* Number 4 omitted in Russian.

SUMMARY

1. Conditions have been found for the reduction at the mercury drop of the nitrile of cinnamic acid, the nitrile of α-phenylcinnamic acid, the dinitrile of fumaric acid, and the azodinitrile of isobutyric acid and the main polarographic characteristics of these compounds have been determined.

2. The direct proportionality between the value of the limiting diffusion currents and the concentration of the nitriles named above has been established.

3. The possibility has been established and the conditions found for the quantitative determination of mixtures of the nitrile of α-phenylcinnamic acid, the dinitrile of fumaric acid, and 2,2'-azobisisobutyronitrile.

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CYCLIC ESTERS OF ANTIMONOUS ACID

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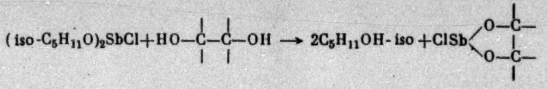
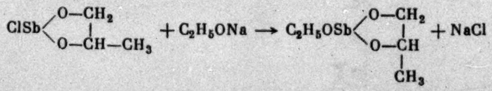
The cyclic esters of antimonous acid have been little investigated.

In 1932 D. Clark [1] obtained the acid chloride of the ethylene glycol cyclic ester of dithioantimonous acid (2-chloro-1,3,2-dithiastibiolane) and, hence, a number of other derivatives of this acid. Somewhat later, Brown and Austin [2] synthetized some derivatives of 2-hydroxybenzodioxastibiole.

In this paper we present some results on the synthesis of acid chlorides and alkyl esters of cyclic esters of antimonous acid. The best method of obtaining the acid chlorides was by exchange-esterification, a method which we used before for the preparation of dialkoxychlorostibines [3]. By the interaction of equimolecular quantities of diisoamylchlorostibine with ethanediol, propanediol and n-butane-1,3-diol we obtained respectively 2-chloro-1,3,2-dioxastibiolane, 2-chloro-4-methyl-1,3,2-dioxastibiolane and 2-chloro-1,3,2-dioxastibinane.



These were white crystalline substances which rapidly hydrolyzed in air to give antimonous oxychloride; they decomposed on heating. 2-Chloro-4-methyl-1,3,2-dioxastibiolane reacted with sodium ethoxide in alcohol to give 2-ethoxy-4-methyl-1,3,2-dioxastibiolane.

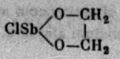
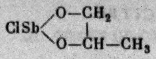
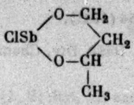
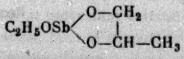


We did not succeed in obtaining 2-ethoxy-1,3,2-dioxastibinane in a pure form, since it decomposed when heated to distill it, and did not come out of solution when attempts were made to recrystallize it. The esters synthetized are shown in the table.

EXPERIMENTAL

Preparation of 2-chloro-1,3,2-dioxastibiolane. Diisoamylchlorostibine (20.0 g) was placed in a Wurtz flask, and 3.8 g of ethanediol was added slowly.

The mixture was heated for 1 hour on a water bath. Isoamyl alcohol was distilled off under reduced pressure at 50-52° (30 mm); it weighed 9.6 g and had the following properties: b.p. 131-132°, d 0.8114. In the flask there remained a white crystalline mass, which decomposed and blackened when an attempt was made to distill it. The white product was soluble in ethyl alcohol, benzene and ether. After recrystallization from ethyl alcohol and drying in a vacuum desiccator at 70-80°, it had a m.p. of 190-194° and blackened on melting. It hydrolyzed in air.

Formula of ester	Melting point	% Sb	
		found	calculated
	190—194°	55.63	56.05
	112—116	52.05	52.66
	160—165	48.69	49.22
	130—133	50.06	50.57

Preparation of 2-chloro-4-methyl-1,3,2-dioxastibiolane. This was synthetized from 20.5 g of diisoamylchlorostibine and 7 g of propanediol under the same conditions as above.

Preparation of 2-chloro-1,3,2-dioxastibinane. This was synthetized from 16.4 g of diisoamylchlorostibine and 4.1 g of n-butane-1,3-diol under the same conditions as above.

Preparation of 2-ethoxy-4-methyl-1,3,2-dioxastibiolane. A solution of 10.5 g of 2-chloro-4-methyl-1,3,2-dioxastibiolane in 30 ml of alcohol was added from a dropping funnel (a small amount of heat was evolved) to a solution of sodium ethoxide, prepared by dissolving 1 g of metallic sodium in 50 ml of ethyl alcohol. The mixture was then heated for 1.5 hours on a boiling water bath. The sodium chloride formed was filtered off, washed with alcohol and ether and dried; yield 2.5 g (calc. 2.5 g). Qualitative analysis showed sodium and chlorine.

Part of the alcohol was distilled off from the filtrate, and the remainder was allowed to stand overnight. White, needle-shaped crystals were deposited. These were recrystallized from ethyl alcohol and dried by heating in a vacuum desiccator. The m.p. was then 130-133°. Qualitative analysis (Beilstein) showed the absence of chlorine.

Preparation of 2-ethoxy-1,3,2-dioxastibinane. A solution of 9 g of 2-chloro-1,3,2-dioxastibinane in 30 ml of alcohol was added from a dropping funnel to a solution of sodium ethoxide, prepared by dissolving 0.84 g of sodium in 50 ml of ethyl alcohol. The mixture was then treated as above.

Sodium chloride was separated, part of the alcohol was distilled off, and the remainder was allowed to stand for a few days. A small amount of crystals was deposited. Qualitative analysis (Beilstein) showed the absence of chlorine. But it was not possible to obtain a pure product for the measurement of properties and for analysis.

Hydrolysis of 2-chloro-1,3,2-dioxastibiolane. 2-Chloro-1,3,2-dioxastibiolane (6 g) and 30 ml of water were mixed in a porcelain beaker. The mixture was heated for 4 hours on a water bath. Water was added to make up for evaporation. The white deposit was filtered off and washed with water and with alcohol and ether. The weight after drying was 4.3 g.

Found %: Sb 69.97. SbOCl. Calculated %: 70.29.

Evaporation of the filtrate gave 1.1 g of a viscous liquid, which was not investigated further.

SUMMARY

1. Some acid chlorides of cyclic esters of antimonous acid have been synthetized by the method of exchange esterification, and their properties have been investigated.

2. It has been shown that these esters hydrolyze to form antimonous oxychloride.

3. It has been found that alkyl esters of the cyclic esters of antimonous acid can be synthetized by double decomposition from the acid chlorides of the cyclic esters and sodium alkylate.

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NEW REGULARITIES IN THE PHYSICOCHEMICAL PROPERTIES OF HYDROCARBONS

III. HEATS OF CRYSTALLIZATION OF n-ALKANES

B. M. Tatevskii

It was shown previously [1, 2] that, for each group of alkanes with a particular form of branching of the carbon chain, such properties as molecular volume and refraction, heat of formation from atoms and simple compounds, heat of combustion, heat of evaporation, logarithm of vapor pressure, etc., vary linearly with the number of n-carbon atoms in the alkane.

In this paper we have considered the question of similar regularities in the heats of crystallization of alkanes. Since the data available is very limited, and is only adequate for quantitative analysis in the case of n-alkanes, we have at present confined our considerations to these substances.

As we shall see below, when considering regularities in heats of crystallization, complications arise in connection with the formation of a solid phase which are absent when dealing only with gaseous or liquid phases. The difficulty is that various crystalline modifications may appear, differing either in the packing of the molecules in the crystalline lattice or in the geometrical shape of a given molecule (rotational isomerism) in the crystal. It is obvious that simple regularities between heat of crystallization and number of carbon atoms in the molecule can exist only when the different alkanes crystallize to give the same crystalline form. This is an essential factor when looking for regularities in the heats of crystallization of n-alkanes, since those with even and uneven numbers of carbon atoms in the molecule, and also the higher and lower alkanes, obviously crystallize in different crystalline forms.

Figure 1 shows the relation between the crystallizing temperature of n-alkanes and the number of carbon atoms in the molecule. It is clear from this that the crystallizing temperatures of n-alkanes, with even and uneven numbers of carbon atoms, lie on two different curves, and this indicates that the crystal forms are different for n-alkanes with even and odd numbers of carbon atoms. Similar curves, but less clearly defined owing to the paucity of experimental data, were obtained for 2-methylalkanes.

Consideration showed that, even within each group of n-alkanes (odd or even numbers of carbon atoms), the crystalline modifications formed on crystallization of the liquid were different for alkanes containing different numbers of carbon atoms in the molecule.

Consider first the n-alkanes with odd numbers of carbon atoms, commencing with n-pentane. For the two lowest members of the series (n-pentane and n-heptane) there is no transition point, for the change of the solid phase into another crystalline modification, close to the crystallizing temperature. But for the odd n-alkanes with $n \geq 9$, it is found that, slightly below the crystallizing temperature, there is a transition point for the change of one crystalline form (A) into another (B). Figure 2 shows curves for the crystallizing temperatures (t_{cryst}) and transition temperatures (t_{trans}) of n-alkanes with odd values of n.

If L_A is the heat of crystallization of the liquid into modification A, and L_{AB} is the heat of conversion of form A into form B, then the heat of crystallization of the liquid directly into form B will be*

$$L_B = L_A + L_{AB}. \tag{1}$$

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*A term containing the specific heats of the two phases is neglected, since $t_{cryst.\,A}$ and $t_{trans.\,A\to B}$ are close together.

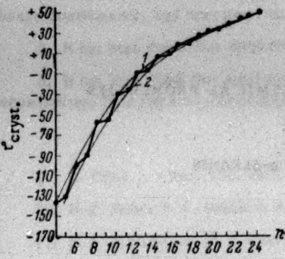

Fig. 1. Variation of the crystallizing temperature (t_{cryst}) of n-alkanes with the number (n) of carbon atoms in the molecule. 1) n even, 2) n odd.

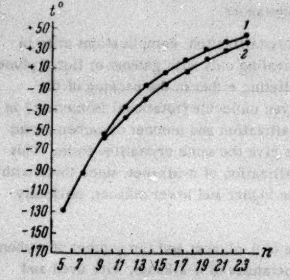

Fig. 2. Variation of the crystallization temperature (t_{cryst}) (1) and the transition temperature (t_{trans}) (2) for n-alkanes with odd values of n.

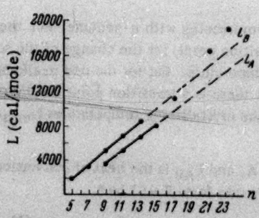

Fig. 3. Variation of heats of crystallization of n-alkanes with odd values of n for crystalline modifications A and B.

It is obvious that, for odd alkanes with n ≥ 9, linear relations may be expected between L_A and n and between L_B and n, though, in general, the two linear relations may be different.

$$L_A = \alpha_A + \beta_A \cdot n$$
$$L_B = \alpha_B + \beta_B \cdot n \qquad (2)$$

Figure 3 shows that linear relations do apply for n ≥ 0. It is also evident from the figure that the observed values of the heats of crystallization of liquid n-pentane and n-heptane (n < 9) fall on the line relating L_B and n, which indicates that these hydrocarbons crystallize in form B and not in form A.

Table 1 shows values of α_A, β_A and α_B, β_B, calculated from the experimental data [3]; Table 2 shows the experimental values of L_A and L_B [3] compared with those calculated from Equation (2), using the values of α_A, β_A and α_B, β_B given in Table 1.

For n-alkanes with values of n > 20, the experimental values of L_A and L_B are probably very imprecise, since the measurements were made on samples of uncertain purity. We believe the values calculated from Equation (2) to be more reliable. The value of L_A for n-heptadecane is also doubtful, since L_{AB} (and consequently L_B) have not been determined for this hydrocarbon, and the experimental value of L_A is closer to the calculated L_B than to the calculated L_A. Probably the experimental result was an average between L_A and L_B, or a value closer to L_B.

For alkanes with even values of n, with 5 < n < 20, no transition points have been observed for the change from one crystalline form to another, during crystallization of the liquid. But they have been observed when n< 5 or > 20, with t_{trans} slightly below t_{cryst} (Fig. 4). Probably all the liquid n-alkanes with 5 < n < 20 crystallize into the same crystalline modification (C). There should be a linear relation between n and the heat of crystallization, L_C, of this modification for 5 < n < 20.

$$L_C = \alpha_C + \beta_C \cdot n \qquad (3)$$

Figure 5 shows that there is such a linear relation. For the higher alkanes with even values of n > 20, which can exist in the solid phase in two crystalline forms (the second form is called D), the experimental values [3] of L_C and L_D are clearly very imprecise, since they were obtained with samples of unknown purity, and showed no regular trend. For this reason, heats of crystallization $L' = L_{cryst}$ and $L'' = L_{cryst} + L_{trans}$ are not shown in Table 2 for even values of n > 20. For n-butane, $L'' = L_{cryst} + L_{trans}$ is satisfactorily expressed by Equation (3), so that it appears that it is modification C which exists below t_{trans}.

TABLE 1

Values of the Constants α and β (kcal/mole) for Calculating Heats of Crystallization of n-Alkanes into Different Crystalline Forms

	L_A		L_B		L_C	
	α	β	α	β	α	β
n-Alkanes (n odd)	—	—	—	—	−2170	917
n-Alkanes (n even)	−2349	845	−3125	762	—	—

TABLE 2

Experimental [3] and Calculated (Equations (2) and (3)) Values of Heats of Crystallization (kcal/mole) of n-Alkanes into Different Crystalline Modifications.

n-Alkanes (n odd)	L_B		L_A		n-Alkanes (n even)	L_C	
	Experimental	Calculated	Experimental	Calculated		Experimental	Calculated
n-Pentane	2011	1876	—	—	n-Butane	1608	1498
n-Heptane	3356	3566	—	—	n-Hexane	3126	3332
n-Nonane	5198	5256	3697	3733	n-Octane	4957	5166
n-Undecane	6940	6946	5301	5257	n-Decane	6863	7000
n-Tridecane	8643	8636	6812	6781	n-Dodecane	8804	8834
n-Pentadecane	10459	10326	8268	8305	n-Tetradecane	10772	10668
n-Heptadecane		12016	11400 (?)	9829	n-Hexadecane	12753	12502
n-Nonadecane	—	13706	—	11353	n-Octadecane	14450	14336
n-Heneicosane	—	15396	16900 (?)	12877	n-Eicosane	—	16170
n-Tricosane	24800 (?)	17086	19400 (?)	14401	n-Docasane	—	18004
n-Pentacosane	—	18776	18890 (?)	15925	n-Tetracosane	—	19838
n-Heptacosane	—	20466	—	17449	n-Hexacosane	—	21672
n-Nonacosane	—	22156	—	18973	n-Octacosane	—	23506
					n-Triacontane	—	25340

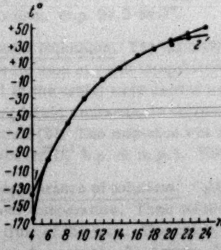

Fig. 4. Variation of the crystallization temperature, $t_{cryst.}$ (1) and the transition temperature, $t_{trans.}$ (2) for n-alkanes with even values of n.

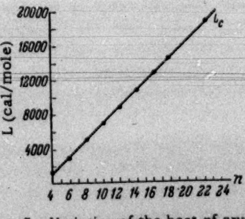

Fig. 5. Variation of the heat of crystallization of n-alkanes with even values of n for crystalline modification C.

Table 1 gives the values of α_C and β_C calculated from the experimental data, and Table 2 shows the experimental and calculated values of L_C. For $n > 20$, we think that the calculated values of L_C are more reliable than the experimental values of L", which must obviously be interpreted as L_C.

SUMMARY

1. The variation of the heat of crystallization of n-alkanes as a function of the number (n) of carbon atoms in the molecule has been considered.

2. It has been shown that the heats of crystallization of the lower members of the n-alkane series are linear functions of n, but the functions are different for odd and even values of n, because the corresponding hydrocarbons crystallize in different crystalline forms.

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THE PROTON MOBILITY OF HYDROGEN ATOMS IN AROMATIC HYDROCARBONS WITH ALIPHATIC SUBSTITUENTS

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The proton mobility of hydrogen atoms means their ability to interchange with deuterium or tritium under the influence of bases enriched with these isotopes, to be replaced by alkali metals, and to take part in such organic reactions as condensation, etc. The degree of mobility depends, not only on the structure of the compound containing the hydrogen atoms, but also on the substances with which they interact and the conditions under which they do so. There are therefore, differences in sensitivity between the various methods of detecting mobility. One of the most sensitive methods is metallization, but the replacement of a hydrogen atom by alkali metal so alters the reactivity of a substance that successive metallization becomes more difficult, even if there is an equivalent C−H bond in the starting material. The method of isotope exchange differs, and this is an advantage, in that all the hydrogen atoms subjected to the experimental conditions can take part in the reaction. The sensitivity of exchange reactions is high enough for strongly protophilic reagents; we therefore, in studying the proton mobility of hydrogen atoms in aromatic compounds with aliphatic substituents employed the isotope method, using a solution of potassium amide in liquid deuteroammonia as deuterating agent [1-5].

EXPERIMENTAL

Preparations. Alkylbenzenes were purified by repeated treatment with sulfuric acid, and were then washed dried and distilled up a column. 1) $C_2H_6C_6H_5$, b.p. 60.1-60.2° at 55 mm, $n^{20}D$ 1.4958. 2) n-$C_3H_7C_6H_5$, b.p. 159°. 3) iso-$C_3H_7C_6H_5$, b.p. 72.2-72.3° at 52.5 mm, $n^{20}D$ 1.4914. 4) n-$C_4H_9C_6H_5$, b.p. 89.3-89.4° at 33.8 mm, $n^{20}D$ 1.4892. 5) tert-$C_4H_9C_6H_5$; product I was synthetized by I. P. Tsukervanik from C_6H_6 and C_4H_9Cl with $AlCl_3$ as catalyst, $n^{20}D$ 1.4927; product II was synthetized from benzene and isobutylene with $H_3PO_4 \cdot BF_3$ as catalyst, b.p. 82.3-82.5° at 45-47 mm, $n^{20}D$ 1.4927. 6) $C_6H_{13}C_6H_5$, b.p. 126.8-126.9°, $n^{20}D$ 1.4872, d^{20}_4 0.8576. 7) $C_6H_5(CH_2)_2C_6H_5$, m.p. 52°. 8) $C_6H_5(CH_2)_3C_6H_5$, $n^{20}D$ 1.5560. 9) $C_6H_5(CH_2)_4C_6H_5$, m.p. 52°. 10) $(C_6H_5)_2CHCH_3$, b.p. 268-270°, $n^{20}D$ 1.5760. 11) $(C_6H_5)_3CCH_3$; product I was synthetized by the action of CH_3I on $(C_6H_5)_3CNa$ in liquid ammonia [6] and recrystallized several times from alcohol, m.p. 94.5°; product II was synthetized by E. N. Iurygina by the Grignard reaction, from $(C_6H_5)_3CBr$ and CH_3I, and recrystallized from alcohol, m.p. 94.2-94.7°.

Experimental technique. The experiments were performed using the accepted laboratory method [7]. Glass ampules were used at room temperature and stainless steel ampules at 100-120°. Some control experiments (marked "glass" in the table) were carried out at 120° in glass ampules. These were sealed and placed in a steel vessel containing liquid ammonia, to compensate for the pressure developed. Isotopic analysis was carried out by the drop method [8]. The substance was redistilled under reduced pressure before combustion, and its physical constants checked ($n^{20}D$, b.p. or m.p.). The constants did not change.

Outward appearance of solutions. $C_6H_5(CH_2)_4C_6H_5$ and $(C_6H_5)_3CCH_3$ were only slightly soluble in liquid ammonia at room temperature. Their solubilities at 100-120° were unknown. The other substances were in solution at the time of the tests. The colors of the solutions at the end of the experiments were as follows: 1,3,4,5 – yellow; 6 – orange; 2 – brown; 7-10 – red.

Substance No.	Substance	Temperature	Time in hours	m_A/m_S	Concn. of KND_2 (normality)	c_A°	c_S	αn	n
1	$C_6H_5CH_2CH_3$ $H_{Ar}=5,\ H_\alpha=2,\ H_\beta=3$	v. t.	200	50	0.8	4.88	3.21	6.77	7.4
		v. t.	1400	60	0.8	6.00	4.04	6.93	7.5
		100ᶜ	14	80	0.8	6.00	4.28	7.31	7.9
		120 g.	50	50	0.7	4.73	4.03	9.00	9.7
		120 g.	50	60	0.7	4.73	4.32	9.70	10.3
		120	50	50	0.7	4.73	4.32	9.70	10.4
		100	200	80	0.8	4.10	3.76	9.50	10.2
		100	225	60	0.8	4.10	3.72	9.56	10.3
2	$C_6H_5CH_2CH_2CH_3$ $H_{Ar}=5,\ H_\alpha=2,\ H_\beta=2$	v. t.	50	50	0.8	5.00	2.56	6.30	6.9
		v. t.	1600	130	0.8	5.21	2.59	6.11	6.7
		v. t.	9 мес.	70	0.8	5.00	2.49	6.07	6.6
		100	200	160	0.8	5.21	2.80	6.50	7.0
		100	300	110	0.8	5.21	3.21	7.50	8.1
		100	380	90	0.8	5.00	3.34	8.22	8.8
		100	350	40	0.8	5.00	3.16	7.94	8.5
3	$C_6H_5CH(CH_3)_2$ $H_{Ar}=5,\ H_\alpha=1,\ H_\beta=6$	v. t.	150	60	0.8	4.88	2.33	5.82	6.3
		v. t.	500	100	0.8	4.88	2.36	5.86	6.4
		100 g.	100	50	0.8	4.10	2.72	8.23	8.8
		100 g.	100	50	0.8	4.10	2.63	8.03	8.6
		100	110	60	0.8	4.10	3.66	11.43	12.2
		100	210	60	0.8	4.10	3.62	11.30	12.1
4	$C_6H_5CH_2CH_2CH_2CH_3$ $H_{Ar}=5,\ H_\alpha=2,\ H_\beta=2,\ H_\gamma=2$	v. t.	40	120	0.8	4.88	2.24	6.58	7.1
		v. t.	1500	130	0.8	4.88	2.30	6.65	7.2
		100 g.	90	80	0.8	4.10	2.07	7.18	7.7
		100	200	80	0.8	4.10	2.24	7.80	8.4
		100	200	80	0.8	4.10	2.33	8.14	8.8
		100	360	50	0.8	4.10	2.33	8.21	8.8
		100—120	1030	40	0.8	4.42	3.08	10.56	11.4
		100—120	1130	40	0.8	4.42	3.25	11.13	12.0
5	$C_6H_5C(CH_3)_3$ $H_{Ar}=5,\ H_\alpha=0,\ H_\beta=9$	v. t. (I)	210	50	0.8	4.88	1.62	4.76	5.1
		v. t. (I)	340	170	0.06	4.60	1.62	4.95	5.4
		v. t. (I)	500	60	0.4	5.34	1.77	4.68	5.1
		v. t. (II)	1000	180	0.02	5.21	1.75	4.72	5.1
		v. t. (I)	3000	190	0.4	5.00	1.86	4.90	5.3
		100 (I)	25	100	0.8	5.00	1.94	5.45	5.9
		100 (I)	130	60	0.8	4.10	2.56	9.06	9.8
		100 (I)	230	80	0.8	4.10	3.30	11.70	12.6
		100 (II)	230	100	0.8	4.10	3.30	11.70	12.6
		100 (II)	360	130	0.8	4.10	3.42	12.00	12.9
		100 (II)	500	50	0.8	5.00	3.72	11.30	12.3
		100 (II)	550	50	0.8	5.00	3.98	12.00	12.9
6	$C_6H_5CH_2CH_2CH_2CH_2CH_2CH_3$ $H_{Ar}=5,\ H_\alpha=2,\ H_\beta=2,\ H_\gamma=2$	100	60	110	2.0	4.42	1.66	6.82	7.3
		100	180	130	2.0	4.42	1.73	7.11	7.7
		100—120	450	150	0.8	6.00	3 12	9.47	10.2
		120	470	100	0.8	6.00	3.42	10.44	11.2
		120	520	100	0.8	6.00	3.66	11.25	12.1
7	$C_3H_5CH_2CH_2C_6H_5$ $H_{Ar}=10,\ H_\alpha=4$	v. t.	320	200	0.02	4.25	4.10	12.90	14.0
8	$C_6H_5CH_2CH_2CH_2C_6H_5$ $H_{Ar}=10,\ H_\alpha=4,\ H_\beta=2$	v. t.	1400	130	0.8	6.00	4.73	13.01	14.1
		110	230	110	0.8	6.00	5.44	15.17	16.3
		110	290	160	0.8	6.00	5.52	15.15	16.3
9	$C_6H_5CH_2CH_2CH_2CH_2C_6H_5$ $H_{Ar}=10,\ H_\alpha=4,\ H_\beta=4$	100	130	180	0.8	5.00	3.52	12.90	13.9
		100	300	160	0.8	5.21	3.57	12.60	13.6
		100	500	200	0.8	5.00	3.48	12.73	13.7

(Table continued)

Substance No.	Substance	Temperature	Time in hours	$\frac{m_A}{m_S}$	Concn. of KND₂ (normality)	$c^{\bullet}_A$	c_S	αn	n
10	$(C_6H_5)_2CHCH_3$ $H_{Ar} = 10,\ H_\alpha = 1,\ H_\beta = 3$	v. t.	1400	130	0.8	6.00	3.94	9.38	10.2
		100	14	160	0.8	6.00	4.73	11.27	12.2
11	$(C_6H_5)_3CCH_3$ $H_{Ar} = 15,\ H_\alpha = 0,\ H_\beta = 3$	v. t. (I)	360	400	0.8	5.00	2.20	7.61	8.3
		v. t. (II)	360	510	0.8	5.00	2.81	8.51	9.3
		v. t. (I)	1060	750	0.8	5.00	3.30	11.85	12.9
		100 (II)	25	600	0.8	6.00	5.26	15.92	17.1
		100 (I)	25	920	0.8	5.00	4.57	16.55	17.9
		100 (I)	50	640	0.8	5.00	4.60	16.70	18.0

The experimental results are shown in the table. The symbols have the following meanings: n is the number of atoms of hydrogen replaced by deuterium in the alkylbenzene and phenylalkane molecules: m_A/m_s is the ratio of the numbers of molecules of ammonia and substance; $c_A^{\bullet}$ and c_s are the deuterium concentrations in the water obtained by combustion of the ammonia before the experiment and of the substance after the experiment; α is the distribution coefficient of deuterium ($\alpha_{20°} = 0.92$; $\alpha_{100°} = 0.93$); glass refers to the control tests in glass ampules; r.t. is room temperature; I and II are the products obtained by different methods.

DISCUSSION OF RESULTS

The reaction of metallization of organic compounds was discovered by Shorygin [9]. In the alkylbenzenes it is the hydrogen atoms attached to the α-carbon atom of the alkyl group which are replaced by alkali metal atoms. It is also primarily the hydrogen atoms in the α position (H_α) which take part in the isotopic exchange reaction. At relatively low concentrations of amide, and at room temperature, there is also partial exchange with the hydrogen atoms of the aromatic C−H bonds (H_{Ar}) (it is sometimes necessary to heat the solution). In methylbenzenes the following numbers of hydrogen atoms participate in exchange [3, 5]: $C_6H_5CH_3$ − 8, $C_6H_4(CH_3)_2$ − 10, $C_6H_3(CH_3)_3$ − 12, $C_6H_2(CH_3)_4$ − 14, $C_6H(CH_3)_5$ − 16, $C_6(CH_3)_6$ − 18, and in methylnaphthalenes, $C_{10}H_7CH_3$ − 10, i. e., $H_{Ar.} + H_\alpha$. The same is found to be true for the isotopic exchange of hydrogen in alkylbenzenes, where the number of exchangeable hydrogen atoms depends on the nature of the substituent alkyl group. With a primary alkyl substituent group, the number of exchangeable hydrogen atoms is 7 ($C_2H_5C_6H_5$, n-$C_3H_7C_6H_5$, n-$C_4H_9C_6H_5$). For secondary alkyl substituents, this number drops to 6 ($C_6H_5CH(CH_3)_2$). And with a tertiary alkyl group, as in $C_6H_5C(CH_3)_3$ there are only 5 exchangeable hydrogen atoms. In the case of phenylalkanes, the number of hydrogen atoms exchangeable with deuterium is also $H_{Ar.} + H_\alpha$: $C_6H_5CH_2C_6H_5$ − 12, $C_6H_5(CH_2)_2C_6H_5$, $C_6H_5(CH_2)_3C_6H_5$ and $C_6H_5(CH_2)_4C_6H_5$ − 14, $(C_6H_5)_3CH$ − 16. Similar results [3, 4] were obtained for fluorene − 10, and for partially hydrogenated hydrocarbons: hydrindene and tetralin − 8, phenylcyclohexane − 6.

These rules can be used for determining the branching of alkyl groups.

In prolonged experiments, with some alkylbenzenes at room temperature, n may slightly exceed the sum of $H_{Ar.} + H_\alpha$. We suggest that this is due to the commencement of exchange by the β-hydrogen atoms (H_β). Consequently, at higher temperatures up to 100-120° and at high concentrations of potassium amide, the number of hydrogen atoms participating in exchange is: n-$C_3H_7C_6H_5$ − 9, $C_2H_5C_6H_5$ − 10, iso-$C_3H_7C_6H_5$ − 12, $C(CH_3)_3C_6H_5$ − 13, i. e., $H_{Ar.} + H_\alpha + H_\beta$ (for tert-$C_4H_9C_6H_5$ this sum is 14).

Even more profound exchange has been noted, up to 12 H atoms for n-butyl- and n-hexylbenzenes.

The control experiments, carried out at the higher temperatures in glass ampules, showed that the exchange of β-hydrogen atoms was not catalyzed by the stainless steel, but was due to the protophilic nature of the solution of potassium amide in liquid ammonia.

It may be considered whether the isotopic exchange of a large number of hydrogen atoms is the result of the influence of the aromatic ring on the mobility of hydrogen atoms at the further end of the alkyl group. But it is not possible to answer this question with certainty, since the exchange occurs under severe conditions approaching those for hydrogen exchange in saturated hydrocarbons.

Thus, when heated with a 3 N solution of the amide, for 1300 hours at 110-120°, heptane and hexane exchange about 3 atoms of hydrogen [10, 11].

All the same, we reckon that the mobility of the β-atoms is definitely affected by the aromatic ring. Isotopic exchange occurs considerably more rapidly with mixed aliphatic-aromatic compounds than with alkanes. For example, complete exchange of hydrogen takes place with ethylbenzene, after 50 hours at 120°, in a 0.7 N solution of amide. In addition, the mobility of the hydrogen atoms of the C−H linkages in the β-position increases with increasing number of aromatic rings. This is evident from the fact that, in spite of the poor solubility of triphenylmethylmethane, $(C_6H_5)_3CCH_3$, in liquid ammonia, complete exchange of the hydrogen atoms in this molecule is attained after a time when the exchange of β-atoms in tert-butylbenzene, $C_6H_5C(CH_3)_3$, is only beginning. In sym-diphenylpropane all the hydrogen atoms will exchange with deuterium, but, in sym-diphenylbutane, only the $H_{Ar.} + H_{\alpha}$ atoms do so. It is true that the second compound is less soluble.

It is known from the literature that the aromatic ring and the β-C−H linkages of the aliphatic substituent affect each other's reactivities; thus the rate of bromination of the alkylbenzene depends on the number of C−H linkages in the alkyl group, in the β- as well as in the α-position [12].

This paper gives only the overall characteristics of the proton mobility of hydrogen atoms in mixed aliphatic-aromatic hydrocarbons. We shall subsequently investigate, quantitatively, the relative mobilities of the hydrogen atoms in the CH_3-, $CH_2<$ and $CH\leqslant$ groups and in the aromatic ring of monoalkylbenzenes.

On the basis of the data in this paper on the mobilities of hydrogen atoms in mixed aliphatic-aromatic hydrocarbons, it was possible to obtain a large number of their deuteroderivatives. We prepared some of these and used them for spectroscopic measurements [5].

Our thanks are due to P. N. Manochkina and M. I. Rikhter for assistance, and to A.L. Liberman, E. N. Iurygina, I. P. Tsukervanik and Ia. M. Paushkin for a number of preparations.

SUMMARY

1. In the case of aromatic hydrocarbons with aliphatic substituents (alkylbenzenes, phenylalkanes, etc.) the hydrogen atoms of the aromatic ring, and those linked to the α-carbon atom of the substituent, will exchange with deuterium (when catalyzed by potassium amide in liquid deuteroammonia).

2. Hydrogen atoms, linked to β-carbon atoms of the substituent, show considerably less mobility, and, if they do participate in hydrogen exchange, require higher temperatures and concentrations of amide and a longer time.

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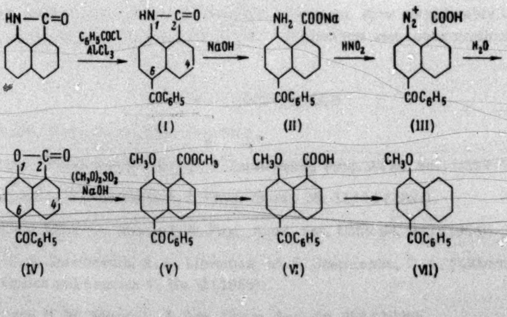
BENZ(cd)INDOLINE DERIVATIVES

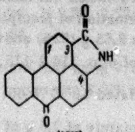
II. 6-BENZOYLBENZ(cd)INDOLINE-2-ONE, 1-METHYL-6-BENZOYLBENZ(cd)INDOLINE-2-ONE AND THE PRODUCTS OF THEIR CYCLIZATION

N. S. Dokunikhin and L. A. Gaeva

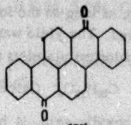
Similar to the known Fritz method of obtaining phenolic ethers is the preparation of aminosubstituted ketones from N-acyl derivatives of aromatic amines, under the influence of aluminum chloride; for instance 4-aminoacetophenone is obtained from acetanilide [1]. Migration of the acyl group to the aromatic nucleus has been described in the case of N-ethylacetanilide [2], and the rearrangement of phthalanil is known [3]. A similar rearrangement might be expected with N-benzoylstyryl. But none was observed when this substance was fused with a mixture of $AlCl_3$ and NaCl at 180°, and tarry matter was formed at higher temperatures. The acylation of naphthostyryl in the aromatic ring, by the Friedel and Crafts method, has not be described. By the action of benzoyl chloride and $AlCl_3$ on naphthostyryl we obtained 6-benzoylbenz(cd) indoline-2-one (I) (using the numbering of [4]). Its structure was shown by its conversion to the already known [5] 4-benzoyl-1-methoxynaphthalene (VII). When (I) was heated with aqueous alkali, a salt of 8-amino-5-benzoylnaphthalene-1-carboxylic acid (II) was obtained. When the diazo derivative (III) of this was boiled with water, 6-benzoylperinaphthofuran-2-one (IV) was formed at once. The furan ring was easily split open by alkali, and the alkaline solution of 8-hydroxy-5-benzoylnaphthalene-1-carboxylic acid reacted with dimethyl sulfate to form the methyl ester of 8-methoxy-5-benzoylnaphthalene-1-carboxylic acid (V). Hydrolysis of this ester gave the free acid (VI), and decarboxylation of this gave (VII). This latter was identical with the substance synthetized from the methyl ether of 1-naphthol and benzoyl chloride, whose structure is well established [5].



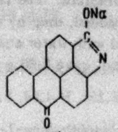
Ring closure, by the method of Scholl, made it possible to proceed from α-benzoyl derivatives of naphthalene to benzanthrone [6]. There was difficulty in converting (I) into the lactam of 4-aminobenzanthrone-3-carboxylic acid (VIII). On fusion with a mixture of $AlCl_3$ and NaCl, particularly when there was oxidation by oxygen or aromatic dinitro compounds, chlorination accompanied ring closure. The formation of chloro derivatives from aromatic amines under these conditions is known [7]. Attempts to obtain VIII, by ring closure with elimination of HCl from 6-(2'-chlorobenzoyl)-benz(cd)indoline-2-one, did not give a positive result. The latter was synthetized from o-chlorobenzoyl chloride and naphthostyryl. It was possible to obtain halogen derivatives of (VIII) free from impurities under conditions such that I was only partially converted, followed by separation of the mixture by crystallization. The lactam of 4-aminobenzanthrone-3-carboxylic acid (VIII) has a structure analogous to that of the golden yellow vat dyestuff – dibenzpyrene quinone (IX). The presence of two carbonyl groups, joined to the system by conjugated bonds, implied that, as with dibenzpyrene quinone, it should be possible to obtain a soluble reduced form (vat) with an alkaline solution of sodium hydrosulfite. But it was found that VIII did not give a vat, because, under the action of alkali, it was converted into a salt of the isomeric form (X), which contained only one C=O group.



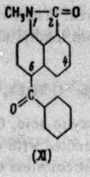
(VIII)



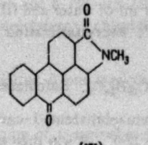
(IX)



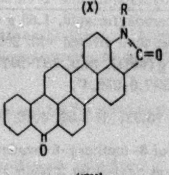
(X)



(XI)



(XII)



(XIII)

This isomerization cannot occur in lactam derivatives with a substituent on the nitrogen atom, and compounds of the type XIII have been described as vat dyestuffs [8]. The action of the methyl ester of benzenesulfonic acid on I gave 1-methyl-6-benzoylbenz(cd)indoline-2-one (XI), and this, on ring closure with $AlCl_3$ and NaCl, gave the partially chlorinated lactam of 4-methylaminobenzanthrone-3-carboxylic acid (XII). This compound gave a red vat in an alkaline solution of sodium hydrosulfite, and dyed cellulose fiber a yellow color, but its affinity for the fiber was insufficient for practical purposes.

EXPERIMENTAL

6-Benzoylbenz(cd)indoline-2-one. Aluminum chloride (30.0 g), a little at a time, and then 15.0 g of naphthostyryl, were added to 20.0 g of benzoyl chloride. The temperature was not allowed to exceed 90°. The mixture was stirred at 90° for 5 hours, by which time it had hardened, and stirring was discontinued. The product was placed in water, acidified with HCl and filtered, and washed with dilute HCl and water. It was then boiled with water a few times to remove benzoic acid. Yield 21.6 g (89%), m.p. 203.4-206.6°; after crystallization from xylene, prisms, m.p. 204.6-205.6°.

Found %: C 79.14, 78.93; H 4.09, 4.12; N 5.11, 5.06. $C_{18}H_{11}O_2N$. Calculated %: C 79.12; H 4.03; N 5.12.

6-(2'-Chlorobenzoyl)-benz(cd)indoline-2-one. Aluminum chloride (23.4 g), a little at a time, and 10.0 g of naphthostyryl at 85-90°, were added to 15.6 g of o-chlorobenzoyl chloride. The mixture was stirred for 4 hours at 90°, transferred to water, filtered and washed with dilute hydrochloric acid and water. The residue was boiled twice with 2 liters of water. Yield 17.46 g (96%), m.p. 239-247°. Recrystallization from xylene gave tapering crystals of m.p. 248.0-251.0°.

Found %: N 4.60, 4.49; Cl 11.47, $C_{18}H_{10}O_2NCl$. Calculated %: N 4.55; Cl 11.54.

6-Benzoyl-perinaphthofuran-2-one. 6-Benzoylbenz(cd) indoline-2-one (20.0 g) was boiled for 3 hours with 100 ml of 10% aqueous NaOH and filtered, and the cold filtrate was treated with 5.0 g of $NaNO_2$ in 30 ml of water. A mixture of 400 g of ice and 100 ml of concentrated hydrochloric acid was added, drop by drop, over a period of 1.5 hours. The mixture was stirred for 1 hour, treated with 100 g of crystalline sodium sulfate and filtered, and the residue was washed with 2% sulfuric acid. The product was added to 200 ml of water with 0.1 g of copper sulfate, boiled for 2 hours, cooled and filtered, and the residue was washed with water and dried. Yield 19.5 g (97%). Recrystallization from butanol gave needles of m.p. 203.6-204.8°.

Found %: C 78.52, 78.69; H 3.59, 3.41. $C_{18}H_{10}O_3$. Calculated %: C 78.83; H 3.68.

Methyl ester of 8-methoxy-5-benzoylnaphthalene-1-carboxylic acid. 6-Benzoyl-perinaphthofuran-2-one (9.0 g), recrystallized from butanol, was added to 150 ml of a 20% aqueous solution of potassium hydroxide, and heated until solution was complete. The temperature of the cold solution was raised gradually from 20 to 50° while dimethyl sulfate was added, drop by drop, as long as the formation of precipitate contnued. The precipitate was filtered off, washed with water and dried. The yield was 8.65 g (82%) and the melting point 109.8-113.0°. Recrystallization from alcohol gave 7.65 g of colorless platelets of m.p. 114.2-115.6°.

Found %: C 75.09, 75.15; H 4.98, 5.14. $C_{20}H_{16}O_4$. Calculated %: C 75.00; H 5.00.

8-Methoxy-5-benzoylnaphthalene-1-carboxylic acid. A mixture of 7.5 g of the methyl ester of 8-methoxy-5-benzoylnaphthalen-1-carboxylic acid, 1.65 g of KOH and 50 ml of ethyl alcohol was boiled under reflux for 16 hours. The mixture was then diluted with 200 ml of water and filtered. The filtrate was acidified with hydrochloric acid. Yield 4.75 g (66%), m.p. 197-207°. Recrystallization from methyl alcohol and chloroform gave colorless prisms of m.p. 207.6-209.4°.

Found %: C 74.11, 73.91; H 4.59, 4.42. $C_{19}H_{14}O_4$. Calculated %: C 74.51; H 4.58.

A mixture of 1.0 g of 8-methoxy-5-benzoylnaphthalene-1-carboxylic acid, 0.2 g of lime and 1.0 g of calcined copper powder was heated for 2 hours at 300°. It was then extracted with chloroform, and the solution was passed through a column packed with alumina. The initially almost colorless effluent was evaporated to remove most of the chloroform, it was then diluted with alcohol, and the rest of the chloroform was distilled off with the alcohol. The residue (2-3 ml) was allowed to stand for 24 hours in a refrigerator and filtered. The yield was 0.2 g of needles of m.p. 78.6-80.0°.

Found %: C 82.82, 82 99; H 5.41, 5.10. $C_{18}H_{14}O_2$. Calculated %: C 82.44; H 5.34.

1-Methoxy-4-benzoylnaphthalene. A mixture of 30.0 g of 1-methoxynaphthalene, 26.9 g of benzoyl chloride, 37.5 g of $AlCl_3$ and 125 ml of carbon disulfide was boiled for 2 hours under reflux, and then added to 250 ml of 10% hydrochloric acid and heated on a steam bath. The solid was heated with a 2% solution of NaOH, washed and dried. Recrystallization from alcohol gave 23.0 g of product of m.p. 78.4-80.2°. According to the literature [5], this method of preparation should give a product of m.p. 82-83°. Purification, by chromatography of the chloroform solution on alumina, gave a product of m.p. 78.8-80.4°, and this was not altered by recrystallization from methanol. A mixture, with a sample prepared by decarboxylation of 8-methoxy-4-benzoylnaphthalene-1-carboxylic acid, also melted at 78.8-80.4°.

Lactam of 4-aminobenzanthrone-3-carboxylic acid. 6-Benzoylbenz(cd) indoline-2-one (2.0 g) was added to a fused mixture of 32 g of $AlCl_3$ and 8 g of NaCl at 155-160° and stirred for 6 hours at 160-165°. The molten reaction mixture was poured on to ice and filtered, and the residue was washed with dilute hydrochloric acid, water and alcohol. The dry residue was heated with 100 ml of xylene, filtered hot and washed on the filter with xylene. The fraction which had not dissolved was recrystallized from 120 ml of trichlorobenzene. Yellow crystals were obtained. Yield 0.6 g, m.p. 350-354° (in metal block).

Found %: C 79.46, 79.50; H 3.30, 3.37; N 5.38, 5.30. $C_{18}H_9O_2N$. Calculated %: C 79.66; H 3.32; N 5.16.

1-Methyl-6-benzoylbenz(cd) indoline-2-one. A mixture of 2.0 g of 6-benzoylbenz(cd) indoline-2-one, 4.0 g of potassium carbonate and 20 ml of trichlorobenzene was heated to 150°, and held at this temperature while a solution of 6.3 g of the methyl ester of benzenesulfonic acid in 12 ml of trichlorobenzene was added over a period of 5 hours. The mixture was filtered, and trichlorobenzene was distilled off in steam from the filtrate.

The product was separated, dried and recrystallized from a mixture of 100 ml of petroleum ether and 50 ml of benzene. Yield 1.1 g (52 %). Pale yellow needles, m.p. 151.0-152.0°.

Found %: C 79.54, 79.55; H 4.47, 4.29; N 4.76, 4.84. $C_{19}H_{13}O_2N$. Calculated %: C 79.44; H 4.53; N 4.87.

1-Methyl-6-benzoylbenz(cd)indoline-2-one (1.0 g) was added to a fused mixture of 16 g of $AlCl_3$ and 4 g of NaCl at 165°, and 0.1 g of m-dinitrobenzene was then added over a period of 1 hour. The mixture was stirred at 165° for 2 hours and poured on to ice. The solid matter was filtered off and washed with dilute hydrochloric acid, water and ethyl alcohol. The dry weight of the product was 0.95 g. Recrystallization from butanol gave yellow polyhedra of m.p. 270-286°. Treatment with sodium hydrosulfite in aqueous caustic soda gave a red vat.

Found %: C 77.73, 77.74; H 3.84, 3.79; N 5.00, 5.06; Cl 2.10, 2.15. $C_{19}H_{11}O_2N$. Calculated % for (XII): C 80.00; H 3.85; N 4.91.

Under the same conditions, but using 0.2 g of 2,4-dinitrochlorobenzene as oxidizing agent, we obtained a product of m.p. 268-283°, containing 3.3% of Cl.

SUMMARY

1. 6-Benzoylbenz(cd)indoline-2-one and 6-(2'-chlorobenzoyl)-benz(cd)indoline-2-one were obtained by the action of benzoyl chloride and o-chlorobenzoyl chloride respectively on naphthostyryl in the presence of $AlCl_3$.

2. 1-Methyl-6-benzoylbenz(cd)indoline-2-one was obtained by the methylation of 6-benzoylbenz(cd)indoline-2-one.

3. We have also synthetized the lactam of 4-aminobenzanthrone-3-carboxylic acid, its partially chlorinated N-methyl derivative, 6-benzoyl-perinaphthofuran-2-one, 8-methoxy-5-benzoylnaphthalene-1-carboxylic acid and its methyl ester.

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CHEMISTRY OF XANTHATES AND VISCOSE

VIII. INVESTIGATION OF POLYTHIO COMPOUNDS AND OF THE COMPOSITION OF VISCOSE, USING LABELLED ATOMS

S. N. Danilov, N. F. Gintse and K. V. Levitskaia

The use of labelled atoms (S^{35}, C^{14}) reveals new possibilities in the investigation of the composition and chemical transformations of viscose, and in particular of the reactions of splitting off of sulfur from the polythio compounds which occur in viscose. It was shown previously [1, 2] that sulfur splitting substances convert dixanthides of cellulose into their thioanhydrides, sodium perthiocarbonate into the trithiocarbonate, sodium disulfide into the monosulfide and sodium thiosulfate into sodium sulfite. Sulfur splitting compounds in viscose are sodium sulfite, sulfide and possibly trithiocarbonate. Sodium cyanide and arsenite are not normally present, but are found to be convenient sulfur splitting agents for the polythio compounds in viscose.

In the experiments described below, we investigated the splitting off, by sodium cyanide and sulfite, of sulfur atoms from dixanthides of cellulose and ethyl alcohol, and from sodium disulfide and perthiocarbonate, all of which contained radioactive sulfur (S^{35}) in their molecule. The results obtained with labelled atoms were compared with those of normal chemical analysis. The use of labelled atoms made it possible to determine both the composition of viscose, particularly the amounts of polythio compounds, and the distribution of the original carbon disulfide among the components.

Determination of transfer of sulfur and of the composition of viscose can be carried out more quickly by the isotopic method than by normal analytical means, but there is the risk of exchange of radioactive and non-radioactive sulfur atoms within a given molecule and between different molecules (isotopic exchange). Isotopic exchange in the case of sulfur compounds may be facilitated by the following reversible reactions:

$$Na_2S_2 + Na_2SO_3 \rightleftarrows Na_2S + Na_2S_2O_3 \tag{1}$$

$$Na_2CS_4 + Na_2SO_3 \rightleftarrows Na_2CS_3 + Na_2S_2O_3 \tag{2}$$

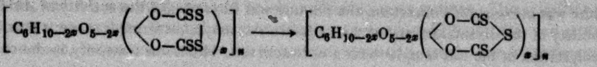
$$Na_2CS_4 + Na_2S \rightleftarrows Na_2CS_3 + Na_2S_2 \tag{3}$$

It has been shown that there is no isotopic exchange at room temperature, in aqueous solution, between sodium sulfide and thiosulfate [3] and between sodium sulfite and thiosulfate [3, 4]; but exchange has been found between ethyl xanthate and elementary sulfur in solution in alcohol-toluene or alcohol-carbon disulfide [5]. The existence of isotopic exchange between sodium sulfide and carbon disulfide [6, 7] is based on indirect evidence, which provides the basis for assuming intramolecular exchange in trithiocarbonates.

When using sulfite as an acceptor of sulfur from polythio compounds containing radioactive sulfur atoms, there are probable complications arising from the splitting off of sulfur by the above reversible reactions; as stated above, loss of radioactive thiosulfate does not occur by isotopic exchange with sulfite.

There is less complication if cyanide is used as a sulfur acceptor. It is known from the literature that there is no isotopic exchange of sulfur with the thiocyanate ion [8].

Dixanthides lose one atom of sulfur to form thioanhydrides:



$$\left[C_6H_{10-2x}O_{5-2x}\left(\left\langle\begin{matrix}O-CSS\\ O-CSS\end{matrix}\right.\right)_x\right]_n \longrightarrow \left[C_6H_{10-2x}O_{5-2x}\left(\left\langle\begin{matrix}O-CS\\ O-CS\end{matrix}\right\rangle S\right)_x\right]_n \qquad (4)$$

By analogy with simple disulfides [9], there is little probability that dixanthides would react with cyanides to give thiocyanates and xanthates.

In our experiments, cellulose dixanthide split off more sulfur than was calculated (from reaction 4), and, according to our results, this was because of the instability of thioanhydrides in alkaline media [10].

We obtained close agreement for the amount of sulfur split off from polythio compounds, using the isotopic and normal methods of analysis, and this showed that there was little isotopic exchange in our experiments. This was confirmed by the following observations: 1) if radioactive polythio compounds were added to viscose, they could be determined with satisfactory precision by the use of sulfur acceptors; 2) if viscose was prepared from xanthate made from radioactive carbon disulfide, and a mixture of disulfide, perthiocarbonate and sulfur acceptor was added, then, after precipitation of the cadmium salts, radioactivity was not observed in the filtrate after 2 hours and only began to appear after several days (these experiments are omitted from the experimental section for the sake of brevity). Since the position of the active sulfur in perthiocarbonate can vary accordingly as active sulfur, active sodium sulfide or active carbon disulfide was used for the preparation, in as much as active preparations are diluted with inactive ones and the capacity to split off sulfur is only inherent in the sulfur atoms of the disulfide group, there are conditions where there can be a loss of activity from perthiocarbonate (in the cadmium precipitate). Further investigation is required on the question of isotope exchange in relation to specific positions of sulfur in perthiocarbonate. Specificity of the sulfur atoms in sodium thiosulfate has been established [11].

The content of polythiocompounds alters during the course of ripening, and reaches 5-7% of the total sulfur in the viscose.

EXPERIMENTAL

The normal methods of synthesis [2] were employed for the preparation of sodium disulfide, perthiocarbonate and dixanthide, with the difference that radioactive elementary sulfur, carbon disulfide and sodium sulfide were used. Since radioactive and inactive reagents were mixed, the polythio compounds obtained were mixtures of substances with different numbers and different positions of radioactive sulfur atoms in their molecules.

In all cases the measurements were made in open cells, using a layer of infinite thickness, a type MST-17 counter with an end window consisting of a thin film of mica, and a type B counter.

1. Investigation of the Splitting off of Sulfur from Dixanthides (experiments by N. F. Gintse, assisted by V. V. Vinogradova)

We investigated the transfer of sulfur from dixanthides of cellulose and of ethyl alcohol to sulfur acceptors (cyanide and sulfite). The amount of sulfur transferred was determined by the labelled atom method and by oxidation.

a) Splitting off of sulfur from cellulose dixanthide. The transfer of sulfur from cellulose dixanthide, labelled with S^{35}, to sodium sulfite and potassium cyanide was followed by measuring the activity of the sodium thiosulfate and potassium thiocyanate formed.

For the preparation of dixanthide containing labelled sulfur atoms, we added a small amount of radioactive carbon disulfide (CS_2^{35}) to the main quantity used for making cellulose xanthate. The active xanthate obtained was freed from byproducts by washing with methyl alcohol, and was converted into the dixanthide by treatment with an aqueous solution of iodine. The resulting dixanthide was washed with water, alcohol and ether, and dried in a vacuum desiccator over phosphorus pentoxide, or in a stream of nitrogen. Because cellulose dixanthide is insoluble in water, and readily decomposes in alkaline solutions, it was necessary to carry out the transfer of sulfur to acceptor under heterogeneous conditions. A given weight of dixanthide was treated with a given volume of an aqueous solution of sodium thiosulfite or potassium cyanide, containing excess of the acceptor. A definite time was allowed for interaction, the mixture was filtered, and the activity of the filtrate was measured. The insolubility of the dixanthide, and of the cellulose thioanhydride formed, made it possible to omit the operation of precipitation of the test sample with a cadmium salt, which was necessary in the case of soluble polythio compounds (see below).

The absence of soluble decomposition products of the dixanthide in the above mentioned filtrates was confirmed by special experiments. It was shown that: 1) the filtrates did not give colored precipitates with acetic acid, 2) the activity of the filtrate did not alter after reprecipitation by a cadmium salt, 3) aqueous and aqueous alcohol extracts, obtained by soaking the original dixanthides for the same time as was used for interaction with acceptor, were inactive. It was therefore concluded that the activity of the filtrates was due exclusively to the activity of sulfur transferred to the acceptor, i. e., to the thiosulfate or thiocyanate in the filtrate.

The activities of the original dixanthide samples were determined in solution in 6-8% caustic soda, using the same concentrations of dixanthide as in the samples which reacted with acceptor. It is known that dixanthides decompose rapidly in alkaline solution, but they do not form volatile sulfur compounds.

TABLE 1

The Action of Sulfur-Splitting Agents on Cellulose Dixanthide

Expt. No.	Acceptor	Time of interaction with acceptor (hours)	Activity (counts/min)		Am't of sulfur transferred (% of original)
			filtrate	orig. dixanthide solution of the same conc.	
1	Sodium sulfite	1.5	100	280	36
	Potassium cyanide	1.5	130	280	46
2	Sodium sulfite	2.5	84	297	28
	Potassium cyanide	2.5	124	297	42
3	Sodium sulfite	0.5	150	420	36
		2.0	140	420	33
		3.0	150	420	36
	Potassium cyanide	0.5	170	420	40
		2.5	190	420	45
4	Sodium sulfite	1.0	110	400	28
		2.0	115	400	29
	Potassium cyanide	1.0	166	400	42
		1.5	154	400	39
		2.0	158	400	40

It is clear, from the data in Table 1, that cellulose dixanthide transfers sulfur to an acceptor comparatively easily and quickly. There was a change from the initial color of the dixanthide even after a few minutes; it changed from pale yellow to grayish green in the presence of sulfite, and to reddish brown in the presence of cyanide. The numerical data shows that the reaction with acceptor was practically complete after 30 minutes, and that potassium cyanide was a more energetic sulfur-splitting agent than sodium sulfite. But the quantity of sulfur split off from the dixanthide was found to be greater than corresponded to its reaction with acceptor to form only thioanhydride. It was 28.36% for sulfite, 39-46% for cyanide (theoretical-25% for the quantitative conversion of dixanthide to thioanhydride). This was rather surprising, as, in earlier experiments [1, 2] on the interaction of dixanthide with potassium cyanide, we obtained yields of about 70% of cellulose thioanhydride (judging by the quantity of potassium cyanide formed, determined argentometrically by Volhard's method), which corresponded to the splitting off of about 18% of sulfur from the dixanthide. The above mentioned control tests may be taken as a sufficient guarantee that there were no sulfur compounds other than thiosulfate or thiocyanate in our filtrates. But, when measuring the activity of solutions of the original cellulose dixanthide, it was found that there was a small but continuous increase with time in the activity of the solution in the measuring layer. A similar phenomenon was subsequently observed with solutions of active preparations of ethyl xanthate and of cellulose thioanhydride, and this was attributed to a flotation effect in these systems. The activities of such systems were taken as the mean of the first and second readings for systems of high activity, and as the first reading, instead of the mean, for systems of lower activity, which required a longer time for measurement.

In order to check the correctness of the values obtained for the proportion of sulfur transferred, in some experiments (Table 2) the activities of both the residue and the filtrate were determined. The residue (of thioanhydride) left on the filter was washed with water, alcohol and ether, dissolved in 6-8% caustic soda, and diluted to the equivalent extent. The instability of thioanhydrides in alkaline media, since it did not lead to the evolution of volatile sulfur compounds, could not have any effect on the determination of the total sulfur by measurement of the activity of the solution. Since there was again some increase in the observed activity when measurements were repeated, the determinations were carried out on the same principle as above for the dixanthide, i. e., the recorded activity was taken as either the mean of the first two measurements, or as the first measurement, depending on the activity of the preparation.

TABLE 2

Distribution of the Sulfur of the Original Cellulose Dixanthide between Acceptor and Residue

Expt. No.	Acceptor	Time of interaction of dixanthide with acceptor (hours)	Activity of solution of original dixanthide (counts/min)	Amount of sulfur (counts/minute)		Total sulfur found (% of original)
				transferred to acceptor	found in residue	
1	Sodium	3	420	150	280	103
	Potassium cyanide	2.5	420	190	220	97
2	Sodium	2.5	340	100	230	98
	Potassium cyanide	2.5	340	150	180	100
3	Sodium sulfite	2.5	316	101	210	98
		4	316	91	210	95
	Potassium cyanide	2.5	316	156	170	103
4	Sodium sulfite	2.5	530	154	376	100
		3.5	530	152	367	98

It is clear from Table 2 that a satisfactory balance was obtained for the distribution of the original dixanthide sulfur between acceptor and residue (the precision of a determination was ± 1-2 %).

In order to counter the suggestion that isotopic exchange might have some effect on the observed amount of sulfur transferred, in spite of the satisfactory overall balance, a supplementary series of experiments was carried out in which the transferred sulfur was determined by oxidation with bromine and alkali. These experiments were performed with nonactive preparations of dixanthide, using the same conditions as above for the interaction of dixanthide with acceptor. The sulfur content of the initial dixanthide was determined by oxidation with bromine and alkali, using samples both of dixanthide and of its solution in 6-8% sodium hydroxide. The oxidation products were precipitated with barium chloride, and the sulfur was determined gravimetrically as barium sulfate. The results agreed for the two starting materials. In order to determine the amount of sulfur transferred to the acceptor the filtrate from the interaction of dixanthide with acceptor was combined with the washings, and an aliquot weight was oxidized. The results of these experiments are shown in Table 3. It will be seen that they agree well with the previous results by the labelled atom method. This confirmed the applicability of our variant of the isotopic method for these systems, and provided indirect evidence of the absence of isotopic exchange of sulfur between the compounds under consideration.

TABLE 3

Distribution of the Sulfur of the Original Cellulose Dixanthide between Acceptor and Residue According to the Results of the Bromide-Bromate Method

Expt. No.	Acceptor	Interaction time (hours)	Sulfur content of original sample of dixanthide (g)	Amount of sulfur (% of original)	
				transferred to acceptor	found in residue
1	Sodium sulfite	2	0.3330	Not determined	66
2	Potassium cyanide	1.5	0.3618	41	60
		3	0.3618	42	57
3	Sodium sulfite	2	0.1427	Not determined	62
	Potassium cyanide	3	0.1427	44	56

b) Splitting off of sulfur from diethyldixanthide. As a result of the interaction of an alcoholic solution of diethyldixanthide with aqueous potassium cyanide, we previously [1] obtained the crystalline thioanhydride of ethyl alcohol in a yield, determined by the thiocyanate formed, equivalent to 77.6% of the theoretical yield of the reaction

$$(C_2H_5OCS_2)_2 + KCN \longrightarrow KCNS + (C_2H_5OCS)_2S \qquad (5)$$

The fact that the yield of diethylthioanhydride was not quite quantitative was attributed by the authors to the ease of decomposition of dixanthide, and particularly of thioanhydride, in an alkaline medium (the pH of a solution of potassium cyanide is about 11).

We did not succeed in raising the yield of thioanhydride by carrying out the reaction in alcohol, because of the poor solubility of potassium cyanide and the high solubility of the thioanhydride in this solvent.

When the reaction was carried out between aqueous potassium cyanide and an alcoholic solution of dixanthide the thioanhydride was obtained in the form of a well crystallized precipitate, and this had a sharp m.p. of 55°* after several recrystallizations from alcohol. From 2 g of dixanthide we obtained 1.1 g of purified diethylthioanhydride, for which the sulfur content found by analysis was 4.61 and 4.83%, compared with the theoretical 4.71%. When the time of interaction of dixanthide and potassium cyanide was increased, the yield of thioanhydride fell markedly, because of its ease of decomposition in a medium of high pH. For instance, if the yield of thioanhydride (unrecrystallized yield by weight from 2 g of dixanthide) was 70% after 40 minutes interaction, this fell to 30% after 7 hours and to 3-4% after 15 hours, while no thioanhydride was obtained when the reactants had stood together for several days.

The previously described method [2] for determining the thiocyanate, formed by the interaction of dixanthide and potassium cyanide, was somewhat modified. Excess of cyanide and unreacted sulfur-containing components were precipitated with a cobalt salt, and the potassium thiocyanate remaining in solutiom was determined, not by the Volhard method, but by potentiometric titration with silver nitrate. Satisfactory precision and good reproducibility were obtained with standard solutions by this method. The titration is easier than by the Volhard method. In our case it was more precise, since it had a transition point with a large and abrupt change of potential. In the Volhard titration it was difficult to see the end point because of the color produced by the excess of cobalt salt. The amount of thiocyanate formed (Table 4) agreed closely with the expected amount of thioanhydride. This was an indication that the interaction of diethyldixanthide with a sufficiently active acceptor occurred with quantitative formation of thioanhydride. As may be seen, the yield of thiocyanate did not depend on the duration of the reaction over the range 0.5 to 1.5 hours. The higher yield of thiocyanate in the experiments with cellulose dixanthide is evidence of the complexity and nonuniformity of the processes of splitting off sulfur from dixanthides of different types.

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* There is an error in the m.p. of diethylthioanhydride given by Danilov and Grad [1] pp. 2194 and 2195; this should be 55° instead of 51°.

The reaction of splitting off of sulfur was evidently accompanied by decomposition of the thioanhydride formed and also of the dixanthide itself.

Additional complications could arise in experiments with cellulose dixanthide because of the heterogeneous conditions.

TABLE 4

Splitting off of Sulfur from Diethyldixanthide in the Reaction between Aqueous Potassium Cyanide and an Alcoholic Solution of Dixanthide

No. of dixanthide batch	Sulfur content of dixanthide sample (m-equiv)	Time of interaction of solutions (minutes)	Amount of sulfur split off	
			in (m-equiv)	in %
1	1.854	30	0.467	25.2
2	0.758	90	0.191	25.2
3	1.289	30	0.343	26.6

2. Splitting off of Sulfur from Sodium Disulfide and Perthiocarbonate [12] (experiments by K. V. Levitskaia).

Sodium disulfide was synthetized from the monosulfide by treatment with sulfur in alcoholic solution: the disulfide crystallized out from the solution in the form of pale yellow crystals ($Na_2S_2 \cdot 5H_2O$). To obtain a radioactive product, 3.6 g of purified monosulfide was mixed with 0.1 g of commercial radioactive monosulfide, and 4.71 g of sulfur, containing 0.0012 g of the radioactive isotope, was used. The product was protected from atmospheric oxygen (nitrogen atmosphere) and light. The product was analyzed for possible traces of thiosulfate, for hydrogen sulfide and for total sulfur. An approximately 0.1 N solution was prepared from the crystalline disulfide, and for each experiment on the loss of sulfur, 5 ml were mixed with 2 ml of 2 N sulfite or cyanide, allowed to stand for a definite time (15, 30, 60, 120 minutes) and then treated with 10% cadmium chloride to precipitate sulfide. The precipitate was filtered off after 5 minutes, and the solution was analyzed, either by measuring its activity, or by determining the content of thiosulfate or thiocyanate. In separate experiments, sodium sulfite was isolated in the form of its formaldehyde compound (Kurtenacker). A blank sample was diluted with water to the total volume of the solution of acceptor and cadmium salt. The activity of the original solution was taken as 100% for calculating the activity of the mixtures. The background was about 40 counts/minute. The statistical error was 3-5%.

Sodium perthiocarbonate was prepared by the interaction of radioactive sodium sulfide and radioactive carbon disulfide, both highly diluted with inactive reagents. It was obtained in the form of a fine crystalline yellow precipitate. A working solution was made up, as in the case of sodium disulfide. Tables 5 and 6 give some examples of the splitting off of sulfur from disulfide and perthiocarbonate by sulfite and cyanide, and these show that the chemical and radioactive methods normally gave good agreement for the amount of sulfur split off, and that sulfite was less effective than cyanide for splitting off sulfur from perthiocarbonate.

3. Determination of the Composition and of the Polythio Compounds of Viscose

In the experiments described below, the splitting off of sulfur from polythio compounds, under the action of sulfur acceptors, was used to determine the total content of polysulfide sulfur in viscose. Sodium sulfite and potassium cyanide were used as acceptors. The transfer of sulfur was followed by chemical and by labelled

TABLE 5

Splitting off of Sulfur from Sodium Disulfide by Thiosulfate and Cyanide

Acceptor	Chemical method		Labelled atom method		
	interaction time (minutes)	sulfur split off (%)	interaction time (minutes)	activity (counts/min)	sulfur split off (%)
Na_2SO_3	30	94	15	685	92
Na_2SO_3	30	87	15	944	90
KCN	—	—	15	532	90
KCN	—	—	15	548	80

TABLE 6

Splitting off of Sulfur from Sodium Perthiocarbonate by Sulfite and Cyanide

No.	Chemical method			Labelled atom method		
	Acceptor	interaction time (minutes)	sulfur split off (%)	interaction time (minutes)	activity (counts/min)	sulfur split off (%)
1	Na_2SO_3	15—120	58	120	258	62
2	Na_2SO_3	15—120	67	120	261	69
3	KCN	—	—	120	229	100
4	KCN	—	—	120	264	96

atom methods. In the latter case, and in the determination of the composition of viscose by the labelled atom method, the experiments were performed with active viscose prepared under laboratory conditions from labelled carbon disulfide. In the other case, the experiments were performed with commercial viscose (for rayon). It would clearly be convenient to use labelled sodium sulfite for measuring the content of polythio compounds in commercial viscose, so as to single out the sulfite from the radioactive thiosulfate formed.

a) We carried out experiments (K. V. Levitskaia) [12] to determine the distribution of carbon disulfide between xanthate and secondary products and the change of this distribution during the course of ripening. Viscose was made from xanthate, prepared from commercial alkali cellulose (10 g cellulose) and technical carbon disulfide (3.5 g), to which active carbon disulfide (0.1 g) CS_2^{35} had been added. At definite time intervals after the xanthate had been dissolved, methanol was used to separate pure xanthate and secondary products. The total activity of the two solutions, of xanthate and secondary products, was taken as 100%, and from the relative activities of the two solutions, it was possible to calculate the percentages of sulfur in the xanthate and in the secondary products. For detailed analysis of the latter, it was necessary to precipitate their cadmium compounds from the filtrate, and to deal with these further by known methods [13]. Omitting details, Table 7 shows the distribution of carbon disulfide in viscose as measured by the labelled atom and normal (Geiger) methods (the difference was 3.2-4.7%).

b) To determine the polythio compounds in a sample of dilute viscose, we (K. V. Levitskaia) added excess of 2 N sodium sulfite, shook thoroughly and, after 15 minutes, added excess of 10% cadmium chloride, which precipitated all of the sulfur compounds except for sodium sulfite, thiosulfate and sulfate. The precipitate of cadmium salts was filtered off and washed with water, until the filtrate gave no reaction with 0.01 N iodine. The filtrate was combined with the washings and, if nonactive viscose had been used, was analyzed for thiosulfate by Kurtenacker's method. In experiments with active viscose, the total radioactivity of the filtrate was measured,

TABLE 7

Distribution of Carbon Disulfide

Labelled sulfur		Iodometric	
xanthate sulfur (%)	secondary product sulfur (%)	xanthate sulfur (%)	secondary product sulfur (%)
62	38	57	43
40	60	37	63

TABLE 8

Determination of Polysulfide Compounds in Viscose by Means of Sodium Sulfite

Viscose	Viscose ripening time (hours)	Method of determination	Sulfur split off (%)
Commercial No. 1	72	Chemical	2.0
Commercial No. 2	48	Ditto	2.0
Active No. 2	0	Isotopic	0
Active No. 2	72	Ditto	4
Active No. 1	41	″	3

TABLE 9

Change in the Content of Polysulfide Compounds in Viscose During Ripening

Viscose No.	Amount of sulfur transferred to cyanide (% of total sulfur content of viscose)						
	ripening time of viscose (days)						
	½	1	2	3	4	5	8
4	—	4.8	4.8	—	5.2	—	6.0
5	4.1	4.1	4.2	4.2	—	4.5	4.8

and this corresponded to the content of thiosulfate and active sulfite split off into solution from the original viscose. The radioactivity of the solution was measured as in the previous experiments. The content of thiosulfate (or of thiosulfate in the total with sulfite) in the original viscose was determined in the same way, by analyzing the filtrate obtained after adding cadmium chloride to the original sample of viscose, which had not been treated with sodium sulfite but had been diluted with water. The difference between these two gave the amount of thiosulfate formed by the splitting off of sulfur from the polythio components of the viscose. The total sulfur content of viscose was determined in the normal way for commercial samples, and for active viscose was obtained from the total activity. The experimental results, given in Table 8, show that 2-4% of the total sulfur in the viscose was capable of reacting with sodium sulfite.

c) Polythio compounds were determined (N. F. Gintse and V. V. Vinogradova) in commercial viscose by means of potassium cyanide. The amount of thiocyanate, formed by the splitting off of sulfur from the polythio components of viscose to cyanide, was determined by potentiometric titration of the filtrate, with silver nitrate and the addition of a cobalt salt. The absolute error was ± 2 % of the amount of sulfur split off. The total sulfur content of the viscose was determined by oxidation with bromine and alkali.

Preliminary experiments established that the reaction between the polythio components of viscose and cyanide was complete within 30 minutes, and that the results did not depend on the degree of dilution of the viscose. When the excess of cyanide was increased to more than 4-fold, there was some increase in the amount of thiocyanate found. When working with standard solutions (sodium disulfide, sodium perthiocarbonate and cellulose xanthate), there was no change in the yield of thiocyanate even when using a 15-20 fold excess of cyanide, although a 1.5-2-fold excess was enough for the completion of the reaction. We therefore used approximately 2 and 4-fold excesses in experiments with viscose.

When sulfite took up 2-4% of the total sulfur of viscose, then the more powerful acceptor – cyanide – took up 4-6%.

It is clear from the data in Table 9 that the content of polythio compounds in viscose increased somewhat with the degree of ripening.

SUMMARY

1. The labelled atom method and the normal analytical means have been used to investigate the splitting off of sulfur from the dixanthides of cellulose and ethyl alcohol, and from sodium disulfide and perthiocarbonate.

2. Thioanhydrides were obtained from dixanthides, but the instability of the former in alkaline solution caused a reduction in yield and increased the percentage of sulfur split off.

3. The labelled atom method made it possible to determine, with sufficient accuracy, the sulfur split off from sodium disulfide and perthiocarbonate under the action of sulfite and cyanide.

4. The labelled atom method, together with the normal analytical technique, made it possible to determine the content of polythio products in viscose during the course of ripening, and the distribution of carbon disulfide between cellulose xanthate and secondary products.

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REACTIONS OF SULFUR AND INORGANIC SULFIDES WITH DIALKYLTRICHLOROPHOSPHINE–ALUMINUM CHLORIDE ADDUCTS

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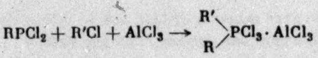
The starting dialkyltrichlorophosphine–aluminum chloride adducts have not been described in the literature until recently. Only very recently [1] has it been reported that in the presence of aluminum chloride alkyldichlorophosphines form solid compounds witn alkyl chlorides. The adducts themselves have not been characterized.

We also obtained these adducts by reacting alkyldichlorophosphine with an alkyl chloride and aluminum chloride according to equation



$$RPCl_2 + R'Cl + AlCl_3 \longrightarrow \begin{matrix} R' \\ R \end{matrix}\!\!>\!PCl_3 \cdot AlCl_3$$

In this manner we obtained aluminum chloride adducts of dimethyl, methylethyl, and diethyltrichlorophosphine. The compounds are white crystals and react readily with many reagents.

We investigated the reactions of these adducts with sulfur and inorganic sulfides. Thus, when they were heated with sulfur or with sulfides of arsenic, antimony, phosphorus, aluminum, and other elements, in the presence of freshly dried (in an oven) potassium chloride, dialkylthiophosphinyl chlorides were formed.

$$R_2PCl_3 \cdot AlCl_3 \xrightarrow{S,\ (Sb_2S_3)KCl} R_2P(S)Cl$$

In this case the potassium chloride was used to tie-up aluminum chloride; this resulted in an appreciably increased yield of dialkylthiophosphinyl chloride.

The physical constants of our dimethyl, methylethyl, and diethylthiophosphinyl chlorides agreed with those reported in the literature for these compounds [2].

EXPERIMENTAL

Dimethyltrichlorophosphine–aluminum chloride adduct. We sealed 13.35 g of aluminum chloride, 11.69 g of methyl dichlorophosphine, and 7.5 g of methyl chloride in a cooled Carius tube (–40°). On attaining room temperature the mixture warmed up spontaneously to 50-60°, and the aluminum chloride dissolved. When cooled, the contents of the tube solidified into a homogeneous, snow white crystalline mass. We obtained 29.2 g (97.2%) of dimethyltrichlorophosphine–aluminum chloride adduct, m. p. 196-198°.

Found %: Cl 70.00, 69.68; P 10.52, 10.39; Al 9.19, 9.30. $C_2H_6Cl_6PAl$. Calculated %: Cl 70.76; P 10.29; Al 8.98.

Methylethyltrichlorophosphine–aluminum chloride adduct. We obtained 30.8 g (98.2%) of this adduct from 11.7 g of methyldichlorophosphine, 13.35 g of aluminum chloride, and 9.6 g of ethyl chloride.

Diethyltrichlorophosphine—aluminum chloride adduct. From 26.18 g of ethyldichlorophosphine, 26.7 g of aluminum chloride, and 19.2 g of ethyl chloride we obtained 64.8 g (98.8%) of diethyltrichlorophosphine—aluminum chloride adduct, m. p. 155-160°.

Found %: P. 9.35, 9.25; Al 8.05, 8.50; C 13.92, 14.67. $C_4H_{10}Cl_7PAl$. Calculated %: P 9.42; Al 8.2; C 14.61.

Dimethylthiophosphinyl chloride. A mixture consisting of 90.3 g of dimethyltrichlorophosphine—aluminum chloride adduct, 9.6 g of sulfur, and 22.3 g of potassium chloride was slowly heated to 200°. The resulting substance was distilled in vacuo. We obtained 19.8 g (48.3%) of dimethylthiophosphinyl chloride.

B. p. 82-83° at 16 mm, $n^{20}D$ 1.542, d^{20}_4 1.2652.

Found %: P 24.55, 24.35; Cl 27.23, 27.34; S 24.60, 24.20. C_2H_6ClSP. Calculated %: P 24.1; Cl 27.61; S 24.9.

Methylethylthiophosphinyl chloride. We obtained 20.6 g (48.4%) of methylethylthiophosphinyl chloride from 94.5 g of methylethyltrichlorophosphine—aluminum chloride adduct, 9.6 g of sulfur, and 22.3 g of potassium chloride.

B. p. 90-91° at 11 mm, $n^{20}D$ 1.5360, d^{20}_4 1.1817.

Found %: Cl 25.02, 24.98; P 21.33, 21.36; S 22.45, 22.49. C_3H_8ClSP. Calculated %: Cl 24.91, P 21.74; S 22.45.

Diethylthiophosphinyl chloride. We obtained 22.9 g (48.9%) of diethylthiophosphinyl chloride from 98.7 g of diethyltrichlorophosphine—aluminum chloride adduct, 9.6 g of sulfur, and 22.3 g of potassium chloride.

B. p. 99-100° at 11 mm, $n^{20}D$ 1.5325, d^{20}_4 1.1542.

Found %: Cl 22.86, 23.17; P 19.58, 19.53; S 20.22, 20.14. $C_4H_{10}ClSP$. Calculated %: Cl 22.64; P 19.85; S 20.44.

Dimethylthiophosphinyl chloride. From 90.3 g of dimethyltrichlorophosphine—aluminum chloride adduct, 20.0 g of antimony pentachloride, and 22.3 g of potassium chloride we prepared 23.8 g (62.0%) of dimethylthiophosphinyl chloride.

B. p. 82-83° at 16 mm, $n^{20}D$ 1.541, d^{20}_4 1.2624.

Found %: P 24.25; 24.09; Cl 27.53, 27.48; S 24.8, 24.75. C_2H_6ClSP. Calculated %: P 24.1; Cl 27.61; S 24.9.

SUMMARY

1. Some aluminum chloride adducts of dialkyltrichlorophosphines were prepared and characterized.

2. It was shown, that a reaction between sulfur or inorganic sulfides and dialkyltrichlorophosphine—aluminum chloride adducts in the presence of potassium chloride resulted in dialkylthiophosphinyl chlorides; at the same time a new way has been found to make dialkylthiophosphinyl chlorides.

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REACTIONS OF SULFUR AND INORGANIC SULFIDES WITH ALUMINUM CHLORIDE ADDUCTS OF ALKYLTETRACHLOROPHOSPHINE

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The alkyltetrachlorophosphine – aluminum chloride adducts described in the literature [1] react readily with many substances to give corresponding derivatives of alkylphosphonic acids. For example, when the adduct reacts with water, alkylphosphonyl chlorides are formed; in the reaction with alcohols, dialkyl esters of alkylphosphonic acids are formed. In the reaction between sulfur and the adducts a 32% yield of alkylthiophosphonyl chloride is obtained [2].

We investigated the reactions of alkyltetrachlorophosphine – aluminum chloride adducts with sulfur and metallic as well as nonmetallic sulfides. Thus, when the above mentioned adducts were heated with sulfur in the presence of freshly dried (in the oven) potassium chloride they gave an 80% yield of alkylthiophosphonyl chloride according to equation

$$RPCl_4 \cdot AlCl_3 \xrightarrow{KCl+S} RP(S)Cl_2 + KCl \cdot AlCl_3 + \text{chlorides of sulfur}$$

Potassium chloride was used to tie-up aluminum chloride. In its absence the yields of alkylthiophosphonyl chlorides decreased to 25-30%.

When the adducts are heated with aluminum, potassium, arsenic, antimony, phosphorus, and other sulfides in the presence of potassium chloride, alkylthiophosphonyl chlorides are formed in 70% yields.

If trichloromethyltetrachlorophosphine – aluminum chloride adduct is heated with sulfur, phosphorus trichloride and carbon tetrachloride are formed; i.e., the adduct decomposes into its original constituents. When this adduct is heated with arsenic or antimony sulfides, carbon disulfide and phosphorus thiochloride are formed.

$$CCl_3PCl_4 \cdot AlCl_3 \xrightarrow[KCl]{Sb_2S_3} CS_2 + PSCl_3$$

The formation of carbon disulfide and phosphorus thiochloride is apparently due to a secondary reaction. At first, a thermal dissociation of the adduct into carbon tetrachloride and phosphorus trichloride takes place. These then react with arsenic and antimony sulfides in the presence of aluminum chloride to give carbon disulfide and phosphorus thiochloride respectively.

Special experiments were set-up to prove this assumption. Thus, if to well mixed antimony pentasulfide and aluminum chloride we gradually add carbon tetrachloride or phosphorus trichloride, an immediate reaction takes place with the formation of carbon disulfide or phosphorus thiochloride respectively, both in good yields.

EXPERIMENTAL

Methylthiophosphonyl chloride. A mixture containing 100.0 g of methyltetrachlorophosphine – aluminum chloride adduct, 9.96 g of sulfur, and 23.17 g of freshly dried (in the oven) potassium chloride was slowly heated to 170°. The resulting reaction products were distilled in vacuo. We obtained 28.2 g (61.0%) of methylthiophosphonyl chloride.

B. p. 69.5-70.5° at 50 mm, $n^{20}D$ 1.5499, d^{20}_4 1.4220.

Found %: P 20.09, 20.50; S 21.04, 21.19; Cl 47.19, 47.33. CH_3Cl_2SP. Calculated %: P 20.78; S 21.52; Cl 47.59.

Ethylthiophosphonyl chloride. From 100.0 g of ethyltetrachlorophosphine–aluminum chloride adduct, 9.52 g of sulfur, and 22.2 g of potassium chloride we obtained 26.3 g (60.5%) of ethylthiophosphonyl chloride.

B. p. 68-69° at 20 mm, $n^{20}D$ 1.5435, d^{20}_4 1.3532.

Found %: P 19.24, 19.01; S 19.50, 19.33; Cl 43.86, 43.73. $C_2H_5Cl_2SP$. Calculated %: P 18.94; S 19.57; Cl 43.73.

Methylthiophosphonyl chloride. From 47.0 g of methyltetrachlorophosphine adduct, 20.0 g of antimony pentasulfide, and 11.0 g of potassium chloride we obtained 14.0 g (64.0%) of methylthiophosphonyl chloride.

B. p. 142-143°, $n^{16}D$ 1.5510, d^{16}_4 1.4185.

Found %: Cl 48.01, 47.98. CH_3Cl_2SP. Calculated %: Cl 47.6.

Reaction of trichloromethyltetrachlorophosphine–aluminum chloride adduct with antimony pentasulfide. A mixture containing 42.4 g of trichloromethyltetrachlorophosphine–aluminum chloride adduct, 15.0 g of antimony pentasulfide, and 7.5 g of potassium chloride were heated on a water bath at 50° for 12 hours, then distilled at atmospheric pressure. We obtained 4.0 g (52.6%) of carbon disulfide, b. p. 45-46°, d^{20}_4 1.2656.

Found %: S 83.6, 84.15; C 16.22, 16.31. CS_2. Calculated %: S 84.15; C 15.78.

We also isolated 7.6 g of phosphorusthiochloride, b. p. 125-126°, d^{20}_4 1.6642.

Found %: S 18.84, 18.82; Cl 62.3, 62.4. $PSCl_3$. Calculated %: S 18.9; Cl 62.77.

Reaction of phosphorus trichloride with antimony pentasulfide in the presence of aluminum chloride. To 40.0 g of antimony pentasulfide and 26.6 g of aluminum chloride we added 27[illegible] g of phosphorus trichloride in small portions. The reaction mixture was then heated for 1 hour at 120° and distilled. We obtained 16.0 g (71.0%) of phosphorusthiochloride, b. p. 124-124.5°, d^{18}_4 1.6659.

Found %: S 18.89, 18.84; Cl 60.74, 60.59, $PSCl_3$. Calculated %: S 18.9, Cl 62.7.

Reaction of carbon tetrachloride with antimony pentasulfide in the presence of aluminum chloride. To 40.0 g of antimony pentasulfide and 10 g of aluminum chloride we added 25.0 g of carbon tetrachloride in small portions. The reaction mixture was then heated for 30 minutes at 50° and distilled. We obtained 8.5 g (69.0%) of carbon disulfide, b. p. 46°, d^{20}_4 1.265.

Found %: S 83.80, 83.75. CS_2. Calculated %: S 84.15.

SUMMARY

1. We investigated the reactions of sulfur and inorganic sulfides with aluminum chloride adducts of alkyltetrachlorophosphine and showed that alkylthiophosphonyl chlorides are formed in these reactions. This also provided a new way of making the latter.

2. When antimony or phosphorus sulfides react with trichloromethyltetrachlorophosphine–aluminum chloride adduct, carbon disulfide and phosphorusthiochloride are formed.

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NEW METHODS OF PREPARING ALKYLDICHLOROPHOSPHINES AND DIALKYLCHLOROPHOSPHINES*

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The literature describes several ways of preparing alkyldichlorophosphines; these ways in general are not very convenient. One of the first methods described was based on the reaction between dialkylmercury and phosphorus trichloride [1]. A known method of preparing aryldichlorophosphones involves a reaction between phosgene and arylphosphines [2]. In the presence of organic peroxides phosphorus trichloride will add to olefins, forming 2-chloroalkyldichlorophosphines [3]. Alkyldichlorophosphines can also be prepared by alkylating phosphorus trichloride with tetraethyl lead [4], or with organocadmium compounds [5].

Only one method of synthesizing dialkylchlorophosphines is known which involves a thermal decomposition of trialkyldichlorophosphines [6, 7]. However, this method is frequently not reproducible.

We have worked out new and convenient methods of preparing alkyldichlorophosphines (I) and dialkylchlorophosphines (II). These methods are based on the reduction of alkyltetrachloro and dialkyltrichlorophosphines-aluminum chloride adducts with metallic aluminum, red phosphorus, and metallic sodium in the presence of freshly dried (in the oven) potassium chloride. The reactions proceed according to equations:

$$
\text{(I)}\quad RPCl_4 \cdot AlCl_3 \begin{cases} \xrightarrow{Al+2KCl} RPCl_2 + 2KCl \cdot AlCl_3 \\ \xrightarrow{P+KCl} RPCl_2 + PCl_3 + AlCl_3 \cdot KCl \\ \xrightarrow{Na} RPCl_2 + NaCl \cdot AlCl_3 \end{cases}
$$

$$
\text{(II)}\quad R_2PCl_3 \cdot AlCl_3 \xrightarrow{Al,\ KCl} R_2PCl + AlCl_3 \cdot KCl
$$

Potassium chloride is used to tie-up aluminum chloride and increases the yields of alkyl and dialkylchlorophosphines considerably. When metallic sodium is used as the reducing agent, potassium chloride is not involved in the reaction, since in this case the sodium chloride formed in the reduction process takes its place.

It should be noted, that powdered aluminum metal turned out to be the most convenient reducing agent. When red phosphorus was used in the reaction, it formed phosphorus trichloride, which complicated the separation of alkyl and dialkylchlorophosphines. The reaction with metallic sodium proceeded very vigorously, sometimes with flashes of fire, and consequently the yields of final products were decreased.

The starting aluminum chloride adducts of alkyltetrachloro and dialkyltrichlorophosphines were available and could easily be prepared from alkyl chlorides, aluminum chloride and phosphorus trichloride or alkyldichlorophosphine respectively [8].

In order to investigate the properties, and also to confirm the structures of dimethyl, methylethyl, and diethylchlorophosphines obtained from the adducts, we added sulfur to them.

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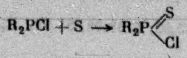
* S. Z. Ivin participated in working out the method of preparing dialkylchlorophosphines.



$$R_2PCl + S \rightarrow R_2P\begin{matrix}\diagup\!\!\!\diagup S \\ \diagdown Cl\end{matrix}$$

We isolated dimethyl, methylethyl, and diethylthiophosphinyl chloride respectively. The constants of the latter agreed with the literature data [7]. Addition of sulfur to dialkylchlorophosphines proceeded considerably easier than addition to alkyldichlorophosphines.

EXPERIMENTAL

Methyldichlorophosphine. We placed into a Claisen flask 50.0 g of methyltetrachlorophosphine–aluminum chloride adduct and 10% of the calculated amount of mixture, consisting of 2.7 g aluminum powder and 23.2 g of freshly dried (in an oven) potassium chloride. The reaction mixture was thoroughly mixed and carefully heated till it began to melt. To the slightly melted reaction mixture we gradually added the remaining 90% of the aluminum and potassium chlorides; at the same time the reaction mixture was being carefully heated. A considerable amount of heat was evolved in the reaction. After the whole amount of mixture ($AlCl_3$ + KCl) was added, the products were distilled. We obtained 13.2 g (72%) of methyldichlorophosphine.

B. p. 81-82° at 760 mm, $n^{20}D$ 1.4960, d^{20}_4 1.3039.

Found %: Cl 60.57, 60.40; P 26.35, 26.44. CH_3Cl_2P. Calculated %: Cl 60.78; P 26.48.

Ethyldichlorophosphine. a) We obtained 26.0 g (67%) of ethyldichlorophosphine from 100 g of ethyltetrachlorophosphine–aluminum chloride adduct, 5.4 g of aluminum powder, and 45 g of potassium chloride.

B. p. 113-114° at 752 mm, $n^{20}D$ 1.493, d^{20}_4 1.2592.

Found %: Cl 54.03, 53.95; P 23.98, 23.86. $C_2H_5Cl_2P$. Calculated %: Cl 54.18; P 23.64.

b) We placed into a Claisen flask 80 g of ethyltetrachlorophosphine–aluminum chloride adduct, then slowly added in small portions 4.92 g of dry red phosphorus, heating the complex meanwhile to its melting point. After the reaction mixture cooled to 15-20°, we added 17.7 g of freshly dried (in an oven) potassium chloride and distilled the mixture. We obtained 22.0 g (70.5%) of ethyldichlorophosphine.

B. p. 113-114° at 752 mm, $n^{20}D$ 1.4928, d^{20}_4 1.2589.

Found %: Cl 54.21, 54.30. $C_2H_5Cl_2P$. Calculated %: Cl 54.18.

c) We placed into a Claisen flask 10.0 g of ethyltetrachlorophosphine–aluminum chloride adduct heated it to 40-60°, and very slowly added 1.37 g of finely dispersed (prepared according to Bruhl) metallic sodium. The reaction proceeded very vigorously with considerable evolution of heat. We obtained 2.7 g (70%) of ethyldichlorophosphine.

B. p. 113-114° at 752 mm, $n^{20}D$ 1.4928, d^{20}_4 1.2588.

Found %: Cl 54.25, 54.34; P 23.68, 23.75. $C_2H_5Cl_2P$. Calculated %: Cl 54.18; P 23.64.

Dimethylchlorophosphine. We obtained 18.5 g of dimethylchlorophosphine from 100 g of dimethyltrichlorophosphine–aluminum chloride adduct, 5.98 g of aluminum powder, and 41.25 g of freshly dried (in an oven) potassium chloride. The boiling point was 77-79° at 756 mm. To this technical grade dimethylchlorophosphine we added sulfur. The resulting dimethylthiophosphinyl chloride had a b. p. 82-83° at 16 mm, and $n^{20}D$ 1.542, d^{20}_4 1.2625; the constants of this compound agreed with those of a sample previously prepared by a different method.

Methylethylchlorophosphine. From 94.5 g of methylethyltrichlorophosphine–aluminum chloride adduct, 5.4 g of aluminum powder, and 37.2 g of freshly dried (in an oven) potassium chloride we obtained 22.7 g (68.3%) of methylethylphosphine. Its boiling point was 100.5-101.5° at 759 mm and 40-41° at 73 mm, $n^{20}D$ 1.474, d^{20}_4 1.0467.

Diethylchlorophosphine. We prepared 25.6 g (66%) of diethylchlorophosphine from 98.7 g of diethyltrichlorophosphine–aluminum chloride adduct, 5.4 g of aluminum powder, and 37.2 g of freshly dried (in an oven) potassium chloride.

B. p. 61-62° at 72 mm, $n^{20}D$ 1.472, d^{20}_4 1.0233.

Found %: Cl 29.06, 29.12; P 24.00, 23.93; C 38.98, 38.97. $C_4H_{10}ClP$. Calculated %: Cl 28.46; P 24.87; C 38.57.

Methylethylthiophosphinyl chloride. To 11 g of methylethylchlorophosphine we slowly added 3.2 g of sulfur. Then the mixture was heated for 40 minutes at 45-50° and distilled in vacuo. We obtained 11.9 g (83.7%) of material.

B. p. 90-91° at 11 mm, $n^{20}D$ 1.531, d^{20}_4 1.1815.

Found %: Cl 25.02, 24.98; P 21.33, 21.36; S 22.45, 22.49. C_3H_8ClSP. Calculated %: Cl 24.91; P 21.74; S 22.45.

Diethylthiophosphinyl chloride. From 12.4 g of diethylchlorophosphine and 3.2 g of sulfur we obtained 13.2 g (84.6%) of diethylthiophosphinyl chloride.

B. p. 93-94° at 6 mm, $n^{20}D$ 1.5286, d^{20}_4 1.1549.

Found %: Cl 22.86, 23.17; P 19.58, 19.53; S 20.22, 20.14. $C_4H_{10}ClSP$. Calculated %: Cl 22.64; P 19.85; S 20.44.

SUMMARY

1. A new method of preparing alkyldichlorophosphines has been worked out; it involves a reduction of alkyltetrachlorophosphine–aluminum chloride adducts with metallic aluminum, red phosphorus, or metallic sodium. We also prepared methyldichlorophosphine, which has not been until now described in the literature.

2. A new method of preparing dialkylchlorophosphines was discovered. The method is based on the reaction between dialkyltrichlorophosphine–aluminum chloride adducts and aluminum metal.

3. We carried out an addition of sulfur to dimethyl, methylethyl, and diethylchlorophosphine and isolated the corresponding compounds, of which the dimethylthiophosphinyl chloride was not previously described in the literature.

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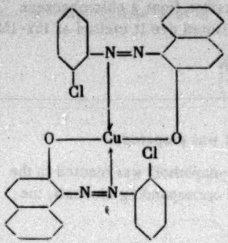
*In Russian.

HALOGEN DISPLACEMENT IN AZO COMPOUNDS

V. REACTION OF THE COPPER COMPLEX OF 2-CHLOROBENZENEAZO-2'-NAPHTHOL WITH ALKOXIDES

M. A. Andreeva and B. I. Stepanov

To explain the mechanism of halogen substitution in o-halo-o'-hydroxyazo dyes in the presence of copper salts [1], it was essential to determine whether it was possible to carry out this reaction in the absence of free copper salts by using a copper complex of the halo dye. With this in mind, we studied the reactions of the copper complex of 2-chlorobenzeneazo-2'-naphthol (azo dye from 2-chloroaniline and 2-naphthol) with n-butyl and benzyl alkoxides.



(I)

The copper complex of the halo dye was prepared by a slightly modified method of G. B. Crippa [2] – heating in acetone (in place of alcohol) with a copper–ammonia solution. Analytical data indicated that the complex contained one copper atom per two dye molecules and, apparently, had the structure (I).

The reactions of complex with sodium butoxide and benzoxide were carried out in solutions of corresponding alcohols for 8 hours at 100-103°. Dyes in which the chlorine was replaced by butoxy and benzoxy groups respectively were isolated in 94.3 and 95.0% yields from the reaction products. Thus, the substitution of chlorine in a copper complex by an alkoxy group proceeded almost quantitatively in the absence of free copper salts. Dyes were identified by mixed melting points.

EXPERIMENTAL

Preparation of the copper complex. We dissolved 5 g of azo dye (made from 2-chloroaniline and 2-naphthol, m. p. 167°, see [1]) in 600 ml of hot acetone. To the cooled solution we added a copper–ammonia solution prepared from 15 g of copper sulfate, 25 ml of 25% ammonia, and 25 ml of water. The mixture was gently refluxed for 2 hours, after which 450 ml of acetone were distilled off. On the following day the precipitate was filtered out, washed with dilute ammonia to remove all traces of copper, then with water and dilute alcohol, after which it was dried to a constant weight. We obtained 5.37 g (96.9%) of complex in the form of greenish-black, shiny flakes, m. p. 252-253°. Complex was insoluble in water, highly soluble in all organic solvents.

Found %: C 61.10, 61.04; H 3.40, 3.45; N 9.05, 9.11. $C_{32}H_{20}O_2N_4Cl_2Cu$. Calculated %: C 61.29; H 3.21; N 8.94.

Reaction of the complex with sodium butoxide. We put 1.57 g of the copper–dye complex into a sodium butoxide solution (prepared by dissolving 0.17 g of sodium metal in 15 ml of n-butyl alcohol (b. p. 117°)), and refluxed the mixture with stirring for 8 hours at 100-103°. The hot reaction mixture was filtered and allowed to stand till the morning. The precipitate that formed overnight (No. 1) was filtered out, washed with a small amount of water and dried (1.42 g); after that, it was refluxed for 1 hour in 50 ml of hydrochloric acid diluted to double its volume. After the solution cooled, the precipitate was filtered out, washed with water to remove chloride ions, and dried. The weight was 1.1 g, m. p. 115.2-116.8°. Chlorine was absent. A sample mixed with known butoxy-substituted dye (m. p. 116-117°, [1]) melted at 116.8-117°.

After the precipitate (No. 1) was filtered out, 0.13 g of another (No. 2) precipitate formed in the filtrate during the following two days. After the above described treatment with HCl it weighed 0.1 g, m. p. 106-113°. Chlorine was absent. The substance was recrystallized twice from acetone, m. p. 118-119.5°. A sample mixed with butoxy-substituted dye melted at 117-119°.

After removal of precipitate (No. 2) the filtrate was evaporated to dryness in vacuo. The residue (greenish-black flakes) was treated as described above.

It weighed 0.31 g, m. p. 90-100°. Chlorine was absent. After two-fold recrystallization from acetone it melted at 116.2-118.5°. Mixed with known butoxy-substituted dye it melted at 117-119°.

The total amount of butoxy-substituted dye obtained was 1.51 g (94.3%).

Reaction of the complex with sodium benzoxide. The amounts of reagents and reaction conditions were the same as before, except that the alcohol was benzyl (b. p. 204-206°). The hot reaction mixture was filtered (filtrate No. 1) and a small amount of residue was washed on the filter with benzyl alcohol till it gave clear filtrates (the residue would not burn). Precipitate No. 1, which formed in filtrate No. 1 after two days, was filtered out, pressed out (filtrate No. 2) washed with water to remove remaining benzyl alcohol, and dried. The weight was 0.96 g, m. p. 149.5-150.5°. Chlorine was absent. After recrystallization from a chlorobenzene–ethyl alcohol mixture it melted at 152-153°. Mixed with known benzoxy-substituted dye (m. p. 152-153°, see [3]) it melted at 152-153.2°.

The filtrate (Nos. 1 and 2) were combined and evaporated in vacuo at 101-103° (bath temperature 110-115°) almost to dryness. The residue was refluxed for 1 hour in 30 ml of two-fold diluted hydrochloric acid, after which the precipitate (No. 2) was filtered out, washed with hot water to remove chloride ions, and dried. The weight was 0.72 g, m. p. 134.7-145°. Chlorine was absent. After two-fold recrystallization from a chlorobenzene ethyl alcohol mixture it melted at 151-153°. Mixed with known benzoxy-substituted dye it melted at 152-153°.

The total amount of benzoxy-substituted dye obtained was 1.68 g (95.0%).

SUMMARY

1. A copper complex of an azo dye from 2-chloroaniline and 2-naphthol was prepared.

2. When the copper complex of the azo dye (from 2-chloroaniline and 2-naphthol) was reacted in the absence of free copper salts with sodium butoxide and benzoxide in solutions of corresponding alcohols, the chlorine was substituted quantitatively by butoxy and benzoxy radicals.

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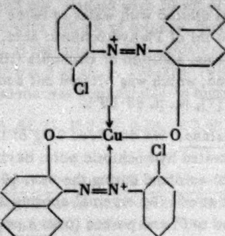
HALOGEN DISPLACEMENT IN AZO COMPOUNDS

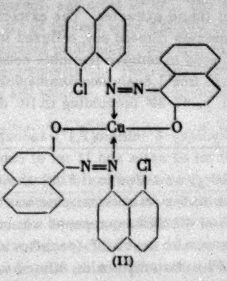
VI. SUBSTITUTION OF CHLORINE BY A METHOXY GROUP IN 2-HYDROXY-8'-CHLORO-(1,1')-AZONAPHTHALENE AND IN ITS COPPER COMPLEX

B. I. Stepanov and V. A. Savel'ev

In a preceeding communication [1] it was shown that when 2-chlorobenzeneazo-2'-naphthol (I) reacted with alkoxides in the absence of free copper salts, chlorine was quantitatively replaced by alkoxy groups. The high activity of chlorine in this complex can be explained by the formation of a positive charge (as a result of participation in a coordinate bond) on the azo nitrogen which is ortho to the chlorine and influences the chlorine–benzene bond strength. If that were so, then the chlorine in a copper complex of 2-hydroxy-8'-chloro-(1,1')-azonaphthalene (II) should not be as active, since the effect of a positively charged nitrogen on the chlorine–naphthalene bond in a periposition would be insignificant.



(I)



(II)

The 1,8-aminochloronaphthalene needed in the synthesis of starting compound, 2-hydroxy-8'-chloro-(1,1')-azonaphthalene (azo dye from 1,8-aminochloronaphthalene and 2-naphthol), was prepared by chlorination of 1-nitronaphthalene in the presence of antimony trichloride, and subsequent reduction of 1,8-nitrochloronaphthalene.

2-Hydroxy-8'-chloro-(1,1')-azonaphthalene was refluxed (72-75°) for 14 hours with sodium methoxide and copper sulfate in a methanol–toluene mixture (1:2 by volume). Under these conditions chlorine was quantitatively replaced by methoxy groups, and the reaction products was separated as a copper complex easily cleaved with boiling hydrochloric acid. Experiments in the absence of copper salts gave negative results. In methanol, without any toluene added, the dye reacted with sodium methoxide much slower, and the reaction took several days, evidently, because of the lower boiling point of the reaction mixture (64-66°). Reduction and cleavage of the 2-hydroxy-8'-methoxy-(1,1')-azonaphthalene gave 1-amino-8-methoxynaphthalene, characterized as N-acetyl derivative.

Thus the data in patent [2], which stated that chlorine in perichloro-o'-hydroxyazo dyes, was as highly active as in o-chloro-o'-hydroxyazo dyes was confirmed.

The copper complex of 2-hydroxy-8'-chloro-(1,1')-azonaphthalene was prepared by Crippa's method [3] – dye was reacted with an copper–ammonia solution in hot methanol. The reaction of copper complex with sodium methoxide was carried out by refluxing them (72-75°) for 15 hours in a methanol–toluene (1:2 by volume) solution and without addition of any free copper salts. The substitution of chlorine by a methoxy group was quantitative. Consequently, we do not exclude the possibility that in the presence of copper salts the replacement of chlorine in perichloro-o'-hydroxyazo dyes in a reaction with alkoxides proceeds through the formation of an intermediate copper complex.

The methoxy-substituted dye obtained can be used to dye acetate fibers by the suspension method.

EXPERIMENTAL

Preparation of 1,8-aminochloronaphthalene. The chlorination of 1-nitronaphthalene was done essentially by the method of Atterberg [4], except that antimony trichloride was used as a catalyst in place of ferric chloride. We heated 150 g of 1-nitronaphthalene (m. p. 58.5°) and 3 g of antimony trichloride to 60° and bubbled chlorine through the melt; bubbling was accompanied by vigorous stirring and continued till the weight of mixture reached 30 g (3.5 hours, 60-70°). The reaction mixture was extracted with 400 ml of hot methyl alcohol, and the insoluble parts were filtered out; on the following day we filtered out the precipitate which formed in methanol on standing, dried and recrystallized it from glacial acetic acid. The weight of product was 65 g, m. p. 89-91°. After another recrystallization from glacial acetic acid we obtained 50 g of 1,8-nitrochloronaphthalene, m. p. 92-92.5° (according to [5], m. p. 94°). After the first and second recrystallization it was possible to isolate from the filtrates and purify 42-45 g (after several recrystallizations) of 1,8-nitrochloronapthalene.

1,8-Nitrochloronaphthalene was reduced by the method of Cason and Wordie [6], except that the quantity of iron powder was increased. We refluxed 40 g of 1,8-nitrochloronaphthalene, 80 g of iron powder, 115 ml of water, and 4 ml of concentrated hydrochloric acid for 8 hours with stirring; during the reaction we added extra 12 ml of hydrochloric acid in 2 ml portions. After the mixture cooled, we added to it 30 ml of 25% ammonia, filtered out the precipitate, and separated 1,8-aminochloronaphthalene from the sludge by extracting it with ethyl alcohol in a Soxhlet liquid extractor. The extract was diluted with water to twice its volume, while the precipitaed amine was quickly filtered out, refluxed in 800 ml of 1% hydrochloric acid. The amine hydrochloride solution was filtered to remove insoluble constituents; addition of ammonia (till the solution became weakly basic) precipitated free 1,8-aminochloronaphthalene, which was filtered out and dried at 40°. The yield was 30 g (90%), m. p. 87-89° (according to lit. data [7], m. p. 88-89°).

Preparation of 2-hydroxy-8'-chloro(1,1')-azonaphthalene. We dissolved 20 g of 1,8-aminochloronaphthalene at 60-70° in 150 ml of water and 11 ml of concentrated hydrochloric acid; having cooled the solution by the addition of ice (50 g) we added to it 8 ml of sulfuric acid and during the next 10 minutes we added 24 ml of 40% sodium nitrate while the reaction mixture was kept at −3° (by external cooling and addition of 100 g of ice). The clear solution of the diazo compound was cooled to 0° and poured (over a period of 30 minutes) into a solution of 2-naphthoxide also kept at 0° (naphthoxide was prepared by heating 20 g of 2-naphthol with 75 ml of water and 30 ml of 30% sodium hydroxide diluted with 75 ml of water); 12 g of sodium carbonate (dried in an oven) had been added to the naphthoxide before the reaction. After being stirred for 30 minutes and standing for 2 hours, the dye was filtered out, refluxed for 20 minutes with 300 ml of 5% sodium hydroxide, filtered while hot, washed with warm water, and dried at 80°. The dry precipitate was refluxed for 20 minutes with 250 ml of methanol, filtered out, dried, and extracted with 125 ml of toluene. The extract was dissolved in 125 ml of methanol, and the dye, which crystallized as thin deep-violet bronzing needles, was filtered out and dried. The yield was 30 g (80%), m. p. 161-162°. 2-Hydroxy-8'-chloro-(1,1')-azonaphthalene was soluble in benzene, toluene, acetone and glacial acetic acid, very slightly soluble in methanol and ethanol, insoluble in water. A solution in concentrated sulfuric acid was violet.

Found %: C 72.11, 71.92; H 4.09, 3.99; N 8.83. $C_{20}H_{13}ON_2Cl$. Calculated %: C 72.12; H 3.93; N 8.42.

Reaction of 2-hydroxy-8'-chloro-(1,1')-azonaphthalene with sodium methoxide. To 30 ml of toluene we added 3 g of 2-hydroxy-8'-chloro-(1,1')-azonaphthalene (initial dye) mixed with 1.5 g of copper sulfate and 2 ml of methyl alcohol; after thorough mixing we added to the mixture 0.7 g of sodium dissolved in 15 ml of methanol. The reaction mixture was refluxed for 15 hours (initial temperature 72°, at the end of reaction 75°), then 3/4 of the solvent were distilled off. On the following day the remainder was extracted with 30 ml of methyl alcohol, the residue filtered out and refluxed for 1 hour with 50 ml of concentrated hydrochloric acid. This mixture was diluted with 30 ml of water; the residue was filtered out, washed to remove chloride ions, and dried at 75°. The yield was 2.6 g (90%). Recrystallization from benzene gave hexagonal violet, bronzing flakes, m. p. 172.5-173° (according to lit. data [8], m. p. 177°). Chlorine was absent. The methoxy-substituted dye was highly soluble in benzene, toluene, acetone and glacial acetic acid, not so soluble in methanol and ethanol, insoluble in water. It gave a violet solution in concentrated sulfuric acid.

Found %: C 76.28; H 5.04; N 8.52. $C_{21}H_{16}O_2N_2$. Calculated %: C 76.81; H 4.91; N 8.53.

We reduced 1.2 g of methoxy-substituted dye dissolved in 10 ml of water by refluxing it with 4 g of stannous chloride and 10 ml of concentrated hydrochloric acid. After decoloration, the reaction mixture was cooled, the precipitate filtered out, and treated with 25 ml of 5% sodium hydroxide plus 0.1 g of sodium hydrosulfite. The part that did not dissolve was separated, washed with a small amount of water and dissolved in a boiling mixture consisting of 10 ml water, 5 ml concentrated hydrochloric acid, and 5 ml methanol. The solution was cleared by boiling with activated charcoal, filtered while hot, and evaporated to half its initial volume. White flaky crystals of 1-amino-8-methoxynaphthalene precipitated, were filtered out and dried at 80°. The yield was 0.7 g. To prepare the N-acetyl derivative we dissolved 0.3 g of 1-amino-8-methoxynaphthalene hydrochloride in 15 ml of water, added to the solution 1 g of sodium acetate dissolved in 10 ml of water, then (with stirring) poured in 5 ml of acetic anhydride. A white crystalline precipitate was filtered out, dried at 60°, and recrystallized from ethanol diluted with an equal volume of water. We obtained 0.3 g of silvery-white, flaky crystals, m. p. 127.5-128° (according to lit. data [8], m. p. 128°). The N-acetyl derivative of 7-amino-8-methoxynaphthalene was highly soluble in ethanol and benzene.

Found %: N 6.48. $C_{13}H_{13}O_2N$. Calculated %: N 6.50.

Preparation of the copper complex of 2-hydroxy-8'-chloro-(1,1')-azonaphthalene. We mixed 4 g of the original dye with 2.5 g of copper sulfate and 2 ml of methyl alcohol and placed them in 50 ml of methyl alcohol; to all this we added 5 ml of 25% ammonia and refluxed for 12 hours (at 66°) with stirring. After cooling, the precipitate was filtered out, washed with 10 ml of methanol, and dried at 75°. The weight was 5.85 g. Precipitate was extracted with 100 ml of toluene, then 60 ml of toluene were distilled off. The deep-violet, powdery copper complex of the original dye, which precipitated on standing, was filtered out the next day and dried at 75°. The weight was 3 g, m. p. 193-194° (with decomposition). The copper complex of 2-hydroxy-8'-chloro-(1,1')-azonaphthalene was high soluble in benzene and toluene, sparingly in methyl alcohol.

Found %: C 66.36, 66.23; H 3.39, 3.54; N 7.68. $C_{40}H_{24}O_2N_4Cl_2Cu$. Calculated %: C 66.07; H 3.32; N 7.70.

Reaction of the copper complex of 2-hydroxy-8'-chloro-(1,1')-azonaphthalene with sodium methoxide. To 1 g of copper complex dissolved in 10 ml of toluene we added a solution of sodium methoxide (0.25 g of sodium in 5 ml of methyl alcohol) and refluxed the mixture for 15 hours (at 72-75°) with stirring. The solvent was distilled off from the reaction mixture and the residue refluxed with 50 ml of concentrated hydrochloric acid for 1 hour; after that, the mixture was diluted with water, the residue filtered out, washed to remove chloride ions, and dried at 75°. The weight was 0.86 g, m. p. 170-172°. Chlorine was absent. After recrystallization from benzene it melted at 172-172.5°; a sample mixed with known methoxy-substituted dye did not lower the melting point. The yield of methoxy-substituted dye was 95.5%.

We want to thank N. N. Borozhtsov for a number of valuable suggestions.

SUMMARY

1. It was established, that when 2-hydroxy-8'-chloro-(1,1')-azonaphthalene reacted with sodium methoxide in the presence of copper salts and under mild conditions (heating on a water bath in a toluene–methanol mixture) chlorine was quantitatively replaced by a methoxy group, and that consequently, a halogen in peri-halo-o'-hydroxyazo dyes was as active as in o-halo-o'-hydroxyazo dyes.

2. The copper complex of 2-hydroxy-8'-chloro-(1,1')-azonaphthalene was obtained and characterized.

3. It was discovered, that in a reaction between the copper complex of 2-hydroxy-8'-chloro-(1,1')-azonaphthalene and sodium methoxide in the absence of free copper salt chlorine was quantitatively substituted by a methoxy group.

4. The method of preparing 1,8-aminochloronaphthalene was perfected.

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**In Russian.

SOME ETHYLENIMINO-1,3,5-TRIAZINES

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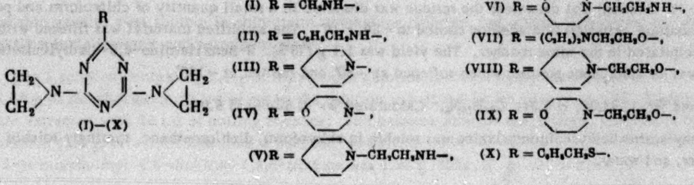
As is known, 2,4,6-triethylenimino-1,3,5-triazine (TET) has already been used for the last 4-6 years to treat certain neoplasms, mainly leukoses. However, the applicability of TET is limited to a large extent by its unusually high toxicity. In search of compounds possessing higher chemotherapeuthic indices, and in continuation of a work published by one of us [1] we synthesized compounds (I)−(X), which were structurally related to TET but contained two ethylenimine groups alongside amino, alkoxy, or alkylmercapto groups.



These compounds were prepared by condensing 2,4-diethylenimino-6-chloro-1,3,5-triazine with corresponding amines or sodium alkoxides and mercaptides in a anhydrous solvent. For the sake of comparison, certain aminodiethyleniminotriazines were also synthesized by condensing corresponding 2-amino-4,6-dichloro-1,3,5-triazines with ethylenimine. In particular, we prepared by the latter method 2-methylamino-4,6-diethylenimino-1,3,5-triazine (I), which had already been described by American workers [2] who synthesized it in a slightly different way.

The synthesized ethyleniminotriazines, when pure, were white crystalline compounds and could be stored at low temperatures for a long time without decomposition. The only exception was 2-benzylamino-4,6-diethylenimino-1,3,5-triazine (II), which was obtained as a white amorphous powder and could not be recrystallized from ordinary solvents.

The biological research on the compounds described in this work was carried out by L. F. Larionov and E. M. Shamaeva in the Chemotherapy Laboratory of our Institute. The results obtained will be reported somewhere else.

EXPERIMENTAL

2-Methylamino-4,6-diethylenimino-1,3,5-triazine (I). A solution containing 2.5 g of 2-methylamino-4,6-dichloro-1,3,5-triazine [3] in 50 ml of benzene was added with stirring at 20-25° to 3.5 ml of ethylenimine dissolved in 50 ml of anhydrous chloroform; the mixture was stirred for 4 hours and left standing overnight. After this, the solution was decanted from the polymer deposited on the walls of the flask, evaporated in vacuo without heating, and the remaining oil was triturated in petroleum ether (40-60° fraction). The resulting solid was recrystallized from benzene−petroleum ether (1:4) mixture; the yield was 0.32 g (12%), m. p. 120-122° (with decomp.). After additional recrystallization from a benzene−petroleum ether (1:2) mixture, m. p. 123-124°.

Found %: C 49.97; H 6.24; N 43.11. $C_8H_{12}N_6$. Calculated %: C 49.93; H 6.29; N 43.73.

The white needle-shaped crystals were soluble in water, benzene, ethyl alcohol, chloroform, and ethyl acetate, slightly soluble in ether.

In the condensation of 2-methylamino-4,6-dichloro-1,3,5-triazine with methylamine in benzene solution we were able to substitute only one chlorine. We dissolved 0.36 g of methylaminodichlorotriazine in 25 ml of anhydrous benzene and added this solution dropwise with stirring at 7-10° to 0.42 ml of ethylenimine dissolved in 5 ml of anhydrous benzene; the mixture was stirred for 2 hours at 25-30° then heated to 75°. Meanwhile, the precipitate which had formed earlier redissolved. The hot solution was filtered, and the filtrate evaporated in vacuo without heating, leaving behind 0.25 g of 2-methylamino-4-ethylenimino-6-chloro-1,3,5-triazine, m. p. 147° (the capillary was lowered into the apparatus at 145°, the temperature rise was 4° per minute). After recrystallization from toluene, m. p. 151°.

Found %: C 38.99; H 4.29; Cl 19.20. $C_6H_8N_5Cl$. Calculated %: C 38.82; H 4.29; Cl 19.10.

The white needles were soluble in chloroform, ethyl acetate, dioxane, sparingly soluble in cold benzene, alcohol, ether, and water.

2-Benzylamino-4,6-diethylenimino-1,3,5-triazine (II). a) To a solution containing 1.34 ml of benzylamine in 20 ml of anhydrous chloroform we added gradually at 5-7° with stirring 1.1 g of 2-chloro-4,6-diethylenimino-1,3,5-triazine dissolved in 20 ml of anhydrous chloroform; the mixture was stirred for 10 more minutes at 8° and 4 hours at 25-27°, then left standing overnight. After that, benzylamine hydrochloride was filtered out, the filtrate evaporated in vacuo without heating, the remaining oil triturated several times in petroleum ether (40-60° fraction) and decanted; the residue was dissolved in a small quantity of chloroform and poured out with constant agitation into acetone cooled to −30, −40°. The solidified material was filtered with suction and reprecipitated in the same manner. The yield was 1.1 g (73%). 2-Benzylamino-4,6-diethylenimino-1,3,5-triazine was an amorphous powder, which softened at ~80° and melted at ~130°.

Found %: C 63.05; H 6.34. $C_{14}H_{16}N_6$. Calculated %: C 62.66; H 6.01.

Benzylaminodiethyleniminotriazine was soluble in chloroform, dichloroethane, sparingly soluble in acetone, ether, and water.

b) We poured (with vigorous stirring) 1.84 g of tricyanogen chloride dissolved in 4 ml of dioxane into 6 ml of water, the solution was cooled to 0° and at 0-5° we gradually added to it a mixture of 1.07 g of benzylamine and 0.4 g of sodium hydroxide dissolved in 10 ml of water; the reaction mixture was stirred for 1.5 hours at 0-5°, and the precipitated substance filtered out and washed with water. The yield of 2-benzylamino-4,6-dichloro-1,3,5-triazine was 2.1 g (80.2%), m. p. 113-117°. We purified the substance by dissolving it in chloroform, filtering, distilling off the solvent and recrystallizing the residue from petroleum ether (40-60° fraction). The melting point was 116.3-117.8°.

Found %: C 47.0; H 3.17; Cl 27.81. $C_{10}H_8N_4Cl_2$. Calculated %: C 47.05; H 3.16; Cl 27.82.

The white needles were insoluble in water, soluble in chloroform, ethyl acetate, and dioxane.

We added at 20° with stirring 0.5 g of benzylaminodichlorotriazine dissolved in 15 ml of anhydrous benzene to 0.47 ml of ethylenimine in 5 ml of anhydrous benzene; the mixture was stirred for 1.5 hours, filtered, and the filtrate evaporated in vacuum. The remaining oil was treated as indicated in Section a. The yield of benzylaminodiethyleniminotriazine was 0.12 g (23%).

2-(N-Piperidyl)-4,6-diethylenimino-1,3,5-triazine (III). a) We condensed in anhydrous chloroform 1.4 g of 2-chloro-4,6-diethylenimino-1,3,5-triazine with 1.55 ml of piperidine in a manner already described for 2-benzylamino-4,6-diethylenimino-1,3,5-triazine. After evaporation of chloroform from the reaction mixture filtrate there remained a crystalline precipitate which was recrystallized from a benzene–petroleum ether (1:3) mixture. The yield of piperidyldiethyleniminotriazine was 1.23 g (70%), m. p. 130-131° (with decomp.). Before analysis the substance was again recrystallized from the same solvents, but the melting point remained unchanged.

Found %: C 58.22; H 7.38; N 34.02. $C_{12}H_{18}N_6$. Calculated %: C 58.51; H 7.36; N 34.12.

The white prismoid crystals were soluble in benzene, chloroform, methylene chloride, and ethyl acetate, insoluble in water and petroleum ether.

b) We added at −8, −13° with stirring 5.7 ml of piperidine in 50 ml of anhydrous ether to 4.8 g of tricyanogen chloride in 100 ml of anhydrous ether; the mixture was stirred for 30 minutes more at −13°, filtered, and the precipitate thoroughly washed with warm ether; the combined filtrates were evaporated to dryness and the residue recrystallized from petroleum ether (40-60° fraction). The yield of 2-piperidyl-4,6-dichloro-1,3,5-triazine was 3.7 g (61%), m. p. 90-90.5°.

Found %: C 41.62; H 4.32; N 24.02. $C_8H_{10}N_4Cl_2$. Calculated %: C 41.22; H 4.32; N 24.03.

Piperidyldichlorotriazine was soluble in ether, benzene, and chloroform, insoluble in water.

To 2.35 ml of ethylenimine in 25 ml of anhydrous benzene we added, at 3-5° with stirring, 2.33 g of piperidyldichlorotriazine in 25 ml of anhydrous benzene; the mixture was stirred for 4 hours more at 30-35°, left overnight, filtered, and the filtrate evaporated in vacuo. After the residue was recrystallized from petroleum ether the yield of piperidyldiethyleniminotriazine was 0.84 g (34%).

2-(N-Morpholinyl)-4,6-diethylenimino-1,3,5-triazine (IV). We condensed 1.97 g of 2,4-diethylenimino-6-chloro-1,3,5-triazine with 1.92 ml of morpholine under conditions described for 2-benzylamino-4,6-diethylenimino-1,3,5-triazine (Section a). After removing chloroform from the filtrate, we triturated the residue in petroleum ether and recrystallized from a benzene−petroleum ether (2.5 : 1.5) mixture. The yield of morpholinyldiethyleniminotriazine was 1.26 g (51%), m. p. 132-133.2° (with decomp.).

Found %: C 53.18; H 6.50; N 33.86. $C_{11}H_{16}ON_6$. Calculated %: C 53.21; H 6.49; N 33.85.

The thin needles were soluble in chloroform, methylene chloride, less soluble in benzene and ethyl acetate, slightly soluble in water and petroleum ether.

b) Into a solution containing 2.4 g of tricyanogen chloride in 50 ml of dry ether we poured at −15° with stirring 2.48 g of morpholine in 25 ml of ether; the solution was stirred for 30 minutes at −15°, filtered, and the precipitate extracted with 20 ml of boiling benzene. The benzene solution was filtered, evaporated in vacuo, and the residue (1.6 g) recrystallized from a benzene−petroleum ether (40-60° fraction) (1 : 1) mixture. The yield of 2-N-morpholinyl-4,6-dichloro-1,3,5-triazine was 1.24 g (40%), m. p. 157.5-158.5°.

Found %: C 35.80; H 3.45; Cl 30.52. $C_7H_8ON_4Cl_2$. Calculated %: C 35.75; H 3.42; Cl 30.19.

The morpholinyldichlorotriazine leaflets were soluble in benzene and chloroform, slightly soluble in ether, and insoluble in water.

We condensed 1.1 g of morpholinyldichlorotriazine with 1.06 ml of ethylenimine in the manner described for 2-piperidyl-4,6-dichloro-1,3,5-triazine. The yield of morpholinyldiethyleniminotriazine was 0.5 g (43%).

2-[β-(N-Piperidyl)-ethylamino]-4,6-diethylenimino-1,3,5-triazine (V). We poured (with stirring) at 10-15° 1.6 g of N-(β-aminoethyl)-piperidine [4] dissolved in 10 ml of anhydrous benzene into a suspension of 1.1 g of 2-chloro-4,6-diethylenimino-1,3,5-triazine in 20 ml of anhydrous benzene and stirred the mixture for 2 more hours at 20-22°. The reaction mixture was filtered, evaporated in vacuo, the resulting viscous oil triturated in petroleum ether, and the solidified substance filtered out. After that, it was dissolved in 10 ml of benzene, filtered, diluted with 20 ml of petroleum ether (40-60° fraction), refluxed with charcoal, filtered, evaporated, and the residue triturated again in petroleum ether. The yield of piperidylethylaminodiethyleniminotriazine was 0.9 g (55.9%), m. p. 81-83°. After a two-fold recrystallization from cyclohexane, m. p. 83.8-85.3°.

Found %: C 58.08; H 7.94; N 34.10. $C_{14}H_{23}N_7$. Calculated %: C 58.10; H 8.01; N 33.88.

The white, thin needles were soluble in water, alcohol, chloroform, and ethyl acetate, practically insoluble in ether and petroleum ether.

2-[β-(N-Morpholinyl)-ethylamino]-4,6-diethylenimino-1,3,5-triazine (VI). This compound was prepared by condensing 2.7 g of N-(β-aminoethyl)-morpholine [4] with 1.85 g of 2,4-diethylenimino-6-chloro-1,3,5-triazine in a manner described for 2-(piperidylethylamino)-4,6-diethylenimino-1,3,5-triazine. The precipitate was dissolved in a petroleum ether−benzene (150 ml and 30 ml) mixture, filtered, and the filtrate was left 24 hours in a refrigerator. The yield was 0.93 g (34%), m. p. 80-81.5° (with decomp.). After another recrystallization from cyclohexane, m. p. 82.1-83.4°.

Found %: C 53.52; H 7.25; N 33.72. $C_{13}H_{21}ON_7$. Calculated %: C 53.55; H 7.26; N 33.63.

The white, cubic crystals were soluble in water, alcohol, chloroform, and ethyl acetate, practically insoluble in ether and petroleum ether.

2-(Diethylaminoethoxy)-4,6-diethylenimino-1,3,5-triazine (VII). We suspended (the usual way) 0.28 g of finely ground sodium metal in 5 ml of xylene, added to the cooled suspension 1.45 g of diethylaminoethanol, heated on a glycerin bath at 70-75° (bath temperature) till sodium almost completely disappeared, cooled, and added to it in small portions 2 g of 2,4-diethylenimino-6-chloro-1,3,5-triazine dissolved in 40 ml of anhydrous benzene. After that, the mixture was refluxed for 2 hours, filtered while hot, and the filtrate evaporated in vacuo (toward the end at 30-35°). The residual light-yellow oil was dissolved in 50-60 ml of hot petroleum ether (40-60° fraction), filtered, and cooled. Diethylaminoethoxydiethyleniminotriazine precipitated from solution in the form of colorless needles, which, after additional recrystallization from petroleum ether, melted at 61.5-62.5°; the yield was 1.83 g (65%).

Found %: C 56.10; H 7.78. $C_{13}H_{22}ON_6$. Calculated %: C 56.09; H 7.97.

The compound was highly soluble in water, alcohol, ether, chloroform, and benzene.

2-[β-(N-Piperidyl)-ethoxy]-4,6-diethylenimino-1,3,5-triazine (VIII). We condensed 3 g of 2,4-diethylenimino-6-chloro-1,3,5-triazine with sodium piperidylethoxide (prepared from 0.37 g of sodium metal and 3.1 g of N-(β-hydroxyethyl)-piperidine) under conditions described for the synthesis of the preceeding compound, dissolved the residue (after evaporation of the reaction mixture filtrate) in 100 ml of ether, filtered, and partially evaporated in vacuo without heating. The yield of piperidylethoxydiethyleniminotriazine was 1.72 g (39%), m. p. 111-112°.

Found %: C 57.85; H 7.66; N 28.59. $C_{14}H_{22}ON_6$. Calculated %: C 57.91; H 7.63; N 28.95.

The compound was highly soluble in alcohol, ethyl acetate, sparingly soluble in ether and petroleum ether.

2-[β-(N-Morpholinyl)-ethoxy]-4,6-diethylenimino-1,3,5-triazine (IX). We added 45 ml of benzene to the alkoxide prepared from 0.39 g of sodium metal and 3.33 g of N-(β-hydroxyethyl)-morpholine in 6 ml of xylene, and to this we added 3 g of diethyleniminochlorotriazine with stirring in such a way as not to raise the temperature of the reaction mixture above 50°; the mixture was stirred for 1 more hour at 50° and left standing overnight. After that, we added to it an equal volume of chloroform, shook it with activated charcoal, evaporated the clear filtrate in vauco, washed the residue on the filter with petroleum ether, and recrystallized from benzene. The yield of morpholinylethoxydiethyleniminotriazine was 2.1 g (47.4%), m. p. 143-145°.

Found %: C 53.35; H 6.92; N 28.51. $C_{13}H_{20}O_2N_6$. Calculated %: C 53.40; H 6.90; N 28.75.

The compound was highly soluble in water, alcohol, and chloroform, sparingly soluble in ether and petroleum ether.

2-Benzylmercapto-4,6-diethylenimino-1,3,5-triazine (X). Sodium mercaptide (prepared under nitrogen from 2 g of benzylmercaptan and 0.38 g of sodium metal in 5 ml of xylene) was condensed (by heating) with 2.53 g of diethyleniminochlorotriazine in 53 ml of anhydrous benzene (bath temperature 80°, time 2 hours), filtered, evaporated in vacuo (without heating) to dryness, and the residue recrystallized from acetone. The yield of benzylmercaptodiethyleniminotriazine was 54%, m. p. 114-115°.

Found %: C 58.89; H 5.41; N 24.22. $C_{14}H_{15}N_5S$. Calculated %: C 58.92; H 5.30; N 24.53.

Benzylmercaptodiethyleniminotriazine was soluble in methyl alcohol, ethyl acetate, and benzene, sparingly soluble in ether and petroleum ether.

SUMMARY

1. In order to study the effect of structural changes in 2,4,6-triethylenimino-1,3,5-triazine on its toxicity and anti-tumor activity, we synthesized: 2-alkylamino-, 2-alkoxy-, and 2-alkylmercapto-4,6-diethylenimino-1,3,5-triazines.

2. The above mentioned compounds were prepared by condensing 2,4-diethylenimino-6-chloro-1,3,5-triazine with amines, alkoxides, and mercaptides respectively.

3. Besides, three aminodiethyleniminotriazines were synthesized in a different way – condensation of corresponding aminodichlorotriazines with ethylenimine.

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SOME DERIVATIVES OF PHENOXAZONE

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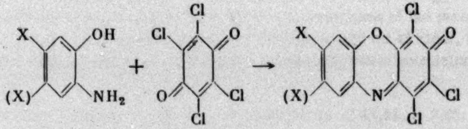
Reaction between chloranil and substituted o-aminophenols leads to the formation of derivatives of phenoxazone (I). This reaction (1) proceeds readily with aminophenols which possess electrophilic substituents (nitro, chloro groups) in the 4th and 5th positions.



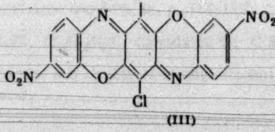
(I)

(1)

The problems connected with the synthesis of nitro-, amino-, and acylamine phenoxazones are not very clearly stated in the literature. In this communication we are reporting the results of research on the synthesis of certain phenoxazone derivatives.

A patent* described a method of preparing technical grade 7-nitro-1,3,4-trichlorophenoxazone-2 (II) by boiling 5-nitro-2-aminophenol with an alcoholic solution of chloranil. We prepared this compound in a 98-99.5% yield by condensing nitroaminophenol with chloranil in an aqueous suspension with the help of surface active agents; such a modification could be useful in preparing compound (II) on an industrial scale. Compound (II), when recrystallized from acetic acid, is a colored product with an intense absorption band in the 480 mμ region (Fig. 1).

7-Nitro-1,3,4-trichlorophenoxazone-2 has an active chlorine in position 3; consequently, two 5-nitro-2-aminophenols can readily react with one chloranil in alcoholic solution to give 2,6-dinitro-9,10-dichlorotriphenyldioxazine (III) in an 83% yield.



(III)

The compound precipitates from chlorobenzene in the form of dark-red needles, which melt above 360°. The absorption spectrum of compound (III) has two characteristic sharp absorption maxima (λ^1_{max} = 490mμ and λ^2_{max} = 530 mμ) in contrast with (II), which only has one maximum (Fig. 1).

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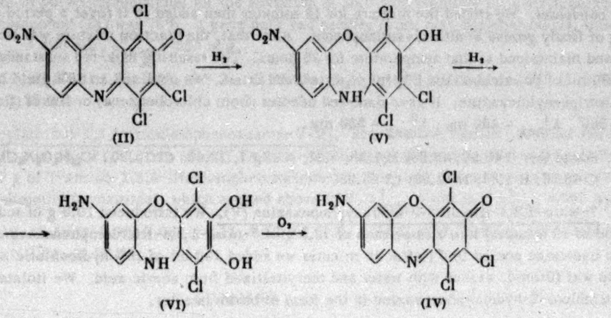
[*] Germ. Pat. 620,346; Friedl. 22,754 (1939).

In the preparation of 7-amino-1,3,4-trichlorophenoxazone-2 (IV) by the reduction of corresponding nitro compound one encounters some serious difficulties. The high activity of chlorine in position 3 excludes reduction with alkali metal sulfides, since the rate of nitro reduction is slower than the halogen–sulfur exchange. Reduction with metals in acidic solutions would not be recommended, due to the great difficulties encountered in separating the product from the ferric sludge. 7-Amino-1,3,4-trichlorophenoxazone-2 can be prepared by the action of sodium hydrosulfide in alkaline solution. As our experiments have shown, formation of compound (IV) proceeds through a series of intermediate steps. We were able to isolate the compounds formed in this process. Thus, when compound (II) was reduced with 1 or 2 moles of sodium hydrosulfite per 1 mole of nitro compounds and the reaction mixture was acidified, an orange colored substance precipitated which crystallized from acetic acid in the form of greyish-brown needles. It analyzed to 7-nitro-1,3,4-trichloro-2-hydroxyphenoxazine (V).

This compound could be converted to compound (IV) by an additional reduction in the presence of air.

However, when we used 4 moles of sodium hydrosulfite per 1 mole of nitro compound and acidified the reaction mixture right after completion of reduction, a white precipitate of 7-amino-1,3,4-trichloro-2-hydroxyoxazine (VI) was formed; it was readily oxidized in air to compound (IV).

The data obtained indicate, that the mechanism by which compound (IV) is formed through the action of sodium hydrosulfite on the nitro compound (in the presence of air) can be represented by sequence (2).



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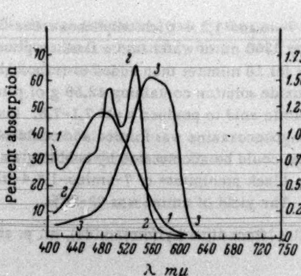

Fig. 1. Absorption waves (acetone solutions).
1) 7-Nitro-1,3,4-trichlorophenoxazone-2 (II); 2) 2,6-dinitro-9,10-dichlorotriphenyldioxazine (III); 3) 7-amino-1,3,4-trichlorophenoxazone-2 (IV).

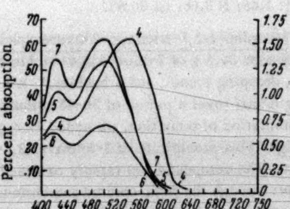

Fig. 2. Absorption waves (acetone solutions).
4) 7-Acetylamino-1,3,4-trichlorophenoxazone-2 (VII); 5) 7-benzoylamino-1,3,4-trichlorophenoxazone-2 (VIII); 6) 7-(3'-nitrobenzoylamino)-1,3,4-trichlorophenoxazone-2 (IX); 7) 7-(4'-nitrobenzoylamino)-1,3,4-trichlorophenoxazone-2 (X).

Compound (IV) crystallizes out as violet needles, which melt above 360°. Replacement of a nitro group by an amino shifts the absorption maximum toward longer wavelengths (λ_{max} 555mμ) (Fig. 1).

Acylation of compound (IV) gives a more intensely colored material. A series of acyl derivatives were prepared by the action of acyl chlorides on compound (IV) at about 160° in polychlorinated benzene solutions.

Light absorption curves for these compounds are drawn in Fig. 2.

EXPERIMENTAL

7-Nitro-1,3,4-trichlorophenoxazone-2 (II). We poured 450 ml of water into a flask supplied with a stirrer, thermometer, and reflux condenser and added 25.8 g of chloranil with a small amount of dispersing agent. We stirred the chloranil suspension for 20 hours, then added to it 17 g of crystalline sodium acetate and (over a period of one hour) 15.4 g of 5-nitro-2-aminophenol. The reaction mixture was heated on a water bath for 7-8 hours at 78-80°. The resulting dark-red substance was filtered out and dried at 80°. The yield was 98.0-99.5%. It gave red needles, m. p. 238-240° (from acetic acid), soluble in chlorobenzene, acetic acid, and dimethylformamide. Its absorption curve had one maximum in the visible range at λ_{max} = 480 mμ.

Found %: C 41.90, 41.84; H 0.96, 1.24; N 8.18, 8.12; Cl 30.60, 30.63. $C_{12}H_3O_4N_2Cl_3$. Calculated %: C 41.71; H 0.88; N 8.10; Cl 30.78.

2,6-Dinitro-9,10-dichlorotriphenyldioxazine (III). We placed 25.48 g of finely ground chloranil, 25.0 g of anhydrous sodium acetate, and 250 ml of ethyl alcohol into a flask supplied with a stirrer, thermometer, and reflux condenser. We stirred the mixture for 10 minutes then added to it (over a period of 1 hour) at 18-20° 33.9 g of finely ground 5-nitro-2-aminophenol. After that, the reaction mixture was slowly heated to its boiling point and maintained at that temperature for 20 hours. The resulting dark-red substance was filtered out, washed with 350 ml of hot alcohol and 500 ml of water, and dried. We obtained an 83% yield of 2,6-dinitro-9,10-dichlorotriphenyldioxazine. It gave dark-red needles (from chlorobenzene) or flakes (from nitrotoluene), m. p. above 360°, λ^1_{max} = 490 mμ, λ^2_{max} = 530 mμ.

Found %: C 48.57, 48.68; H 1.38, 1.21; N 12.57, 12.69; Cl 15.90. $C_{18}H_6O_6N_4Cl_2$. Calculated %: C 48.56; H 1.36; N 12.59; Cl 15.93.

7-Nitro-1,3,4-trichloro-2-hydroxyphenoxazine (V). We introduced 16.0 g of sodium hydrosulfite (over a period of 10 minutes) into a suspension of 13.8 g of 7-nitro-1,3,4-trichlorophenoxazone-2 in 500 ml of 2.5% sodium hydroxide cooled to 0°; after 30 minutes we added 100 ml of 10% hydrochloric acid. The orange precipitate was filtered, washed with water and recrystallized from acetic acid. We isolated 2.6 g of 7-nitro-1,3,4-trichloro-2-hydroxyphenoxazine in the form of brown needles.

Found %: C 41.74, 41.67; H 2.06, 2.04; N 8.49, 8.45; Cl 30.56. $C_{12}H_5O_4N_2Cl_3$. Calculated %: C 41.46; H 1.45; N 8.06; Cl 30.67.

7-Amino-1,3,4-trichloro-2-hydroxyphenoxazine (VI) and 7-amino-1,3,4-trichlorophenoxazone-2 (IV). We introduced 34.5 g of 7-nitro-1,3,4-trichlorophenoxazone-2 and 1300 ml of water into a flask supplied with a stirrer, dropping funnel, and a bubbler.* We stirred the mixture for 10 minutes then added to it through the dropping funnel (over a period of 30-45 minutes) 5% sodium hydroxide solution containing 42.56 g of pure alkali. After completion of reduction, we added 12.4 g of 27.5% hydrochloric acid to produce a pH 7.1-7.8. During this, a light pink precipitate of 7-amino-1,3,4-trichloro-2-hydroxyphenoxazine was formed and could be filtered out. The compound was rapidly oxidized in air. The process could be accelerated by bubbling air for 8-10 hours through the pink colored suspension; the resulting blue black precipitate of 7-amino-1,3,4-trichlorophenoxazone-2 was filtered, washed with water, and dried. The yield of amine was 93-96%.

It gave violet needles (from nitrobenzene) or yellow needles (from dimethylformamide), m. p. above 360°, λ_{max} = 555 mμ.

Found %: C 45.36, 45.68; H 1.83, 1.61; N 8.69, 8.68; Cl 33.89, 33.90. $C_{12}H_5O_2N_2Cl_3$. Calculated %: C 45.70; H 1.58; N 8.88; Cl 33.70.

7-Acetylamino-1,3,4-trichlorophenoxazone-2 (VII). Into a flask supplied with a stirrer, thermometer, dropping funnel, and a reflux condenser we placed 25.0 g of 7-amino-1,3,4-trichlorophenoxazone-2,400 ml (515 g) of polychlorobenzene (155-190° fraction), and heated the mixture with stirring on an oil bath at 140°. At this temperature (over a period of one hour) we added 9.42 g of acetyl chloride dissolved in 80 ml of polychlorobenzenes. The reaction mixture was refluxed for 8 hours. Pressure was slightly reduced to drive off hydrogen chloride formed in the reaction. After completion of acetylation, we cooled the reaction mixture to 90-100°, filtered, washed with 80 ml of hot polychlorobenzenes, and steam-distilled the solvent. The remaining compounds (VII) was filtered, washed with hot water, and dried. The yield was 75-76%. It gave brown needles (from dimethylformamide), which melted above 360°, λ^1_{max} = 430 mμ, λ^2_{max} = 550 mμ.

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* A piece of information is definitely missing here. The nitro group and the carbonyl are being reduced, but no mention is made of the quantity or nature of reducing agent. From earlier information it is certain that $Na_2S_2O_4 \cdot 2H_2O$ was used as reducing agent in a four-fold molar excess (see general discussion) – Publishers note.

Found %: C 47.08, 47.08; H 1.85, 1.88; N 7.98, 7.99; Cl 29.73, 29.45. $C_{14}H_7O_3N_2Cl_3$. Calculated %: C 47.02; H 1.97; N 7.84; Cl 29.75.

7-Benzoylamino-1,3,4-trichlorophenoxazone-2 (VIII). Reaction was carried out in the same way as that for 7-acetylamino-1,3,4-trichlorophenoxazone-2. We used for the acylation 16.9 g of benzoyl chloride. The yield of compound (VIII) was 70%.

Found %: C 54.41, 54.51; H 2.31, 2.44; N 6.71, 6.79; Cl 25.35, 25.42. $C_{19}H_9O_3N_2Cl_3$. Calculated %: C 54.38; H 2.16; N 6.68; Cl 25.35.

7-(3'-Nitrobenzoylamino)-1,3,4-trichlorophenoxazone-2 (IX). The reaction was carried out in a way similar to the one used for preparing the above described acylaminophenoxazone. We used 17.8 g of 3-nitrobenzoyl chloride in 60 ml of polychlorobenzenes for the acylation of 25.0 g of 7-amino-1,3,4-trichlorophenoxazone-2. The yield of compound (IX) was 78%. It gave dark red needles (from polychlorobenzenes), which melted above 360°, λ^1_{max} = 420 mμ, λ^2_{max} = 500 mμ.

Found %: C 49.12, 49.09; H 1.92, 2.73; N 8.75; Cl 22.55. $C_{19}H_8O_5N_3Cl_3$. Calculated %: C 49.11; H 1.74; N 9.04; Cl 22.89.

7-(4'-Nitrobenzoylamino)-1,3,4-trichlorophenoxazone-2 (X). Reaction was carried out under the same conditions as the one with compound (IX). We used 17.8 g of 4-nitrobenzoyl chloride in 160 ml of polychlorobenzene to acylate 25.0 g of 7-amino-1,3,4-trichlorophenoxazone-2. The yield of compound (X) was 83%. It gave red flakes (from dimethylformamide), which melted above 360°, λ^1_{max} = 425 mμ, λ^2_{max} = 500 mμ.

Found %: C 49.10, 49.16; H 2.02, 2.06; N 9.11, 9.19; Cl 22.64, 22.51. $C_{19}H_8O_5N_3Cl_3$. Calculated %: C 49.11; H 1.74; N 9.04; Cl 22.89.

SUMMARY

1. A series of phenoxazone derivatives were synthesized. The absorption spectra of the compounds obtained were determined.

2. It was established that in the process of 7-amino-1,3,4-trichlorophenoxazone-2 formation from the corresponding nitro compound 7-nitro- and 7-amino-2-hydroxy-1,3,4-trichlorophenoxazine were formed as intermediate products.

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DEHYDROGENATION OF α-TETRALONE WITH SELENIUM AND SYNTHESIS OF 1-NAPHTHOL-1-C^{14}

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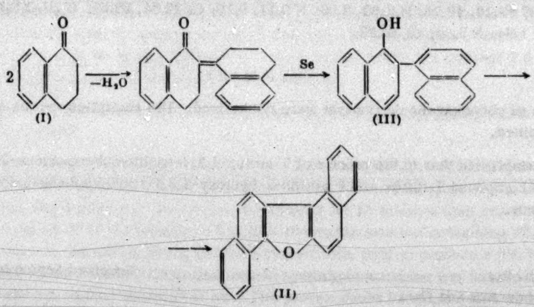
Spiro and co-workers [1] were the first to prepare 1-naphthol-1-C^{14} as a side product (main product–naphthalene-C^{14}) in the dehydrogenation of 1-keto-1,2,3,4-tetrahydronaphthalene-1-C^{14} (α-tetralone-1-C^{14}) at 270° in the presence of palladium-coated carbon. The yield of 1-naphthol-1-C^{14} was only 10%.

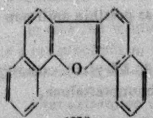
Of the other possible ways of synthesizing this compound the most interesting was the one described by Darzens and Levy [2] – dehydrogenation of α-tetralone (I) with selenium at 330-335° (9 hours). According to the authors' data, this reaction gave a 75% yield of 1-naphthol, whereas dehydrogenation of α-tetralone with sulfur (240°, 4 hours) gave a 40% yield of 1-naphthol.

We checked Darzens' and Levy's data and found out, that, contrary to their assertions, when α-tetralone was heated with selenium for 10 hours at 330° a complex mixture of products resulted in which the yield of 1-naphthol was 25.7%. We also isolated from the mixture α-tetralone (23%), a neutral compound of composition $C_{20}H_{12}O$ (12.2%), and an amorphous substance with phenolic properties. Compound $C_{20}H_{12}O$, judging by its melting point as well as the composition and melting points of its picrate and 1,3,5-trinitrobenzene adduct, was dinaphtho-(1',2':2,3;1",2":4,5)-fumarone (II); its formation could be explained by the following reaction sequence.



Orchin had shown before [3, 4a, b], that during catalytic dehydrogenation it is possible to split-out a hydrogen between a hydroxyl group and a carbon in compounds similar to 2-naphthylnaphthol-1 (III) so as to form derivatives of furan (or pyran).

Besides this, the data of Darzens and Levy can also be refuted by the fact that 1-naphthol can react with selenium to give dinaphtho-(1',2';2,3;2",1":4,5)-furan (IV) (see [5]). Besides, as we will show in the experimental part, after heating the reaction mixture for 10 hours at 330° one can isolate only 15% of the starting 1-naphthol. The yield of dinaphthofuran (IV) in this experiment was 31% (on the basis of impure product).



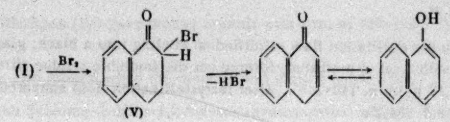
(IV)

It should be noted, that on top of all that was said, the work of Darzens and Levy conflicts with the results of subsequent works on the dehydrogenation of substituted α-tetralones and other cyclic ketones. First of all, none of the investigators [5-8] who carried out similar dehydrogenations with selenium were able to obtain the corresponding phenol in more than a 15% yield; second, dehydrogenation with sulfur usually gives higher yields of phenol than dehydrogenation with selenium [7] (see also [6] and [9]).

The fact that symmetrical dinaphthofuran (IV) was not found among the α-tetralone dehydrogenation products could be explained in the following manner. The formation of dinaphthofuran from 1-naphthol is a bimolecular reaction, and consequently, a lowering in the concentration of the latter should decrease the reaction rate considerably. Therefore, in the case of α-tetralone dehydrogenation, where the concentration of 1-naphthol during the reaction is low, one can not expect any appreciable formation of dinaphthofuran (IV).

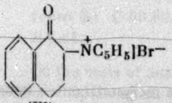
It should be noted that Cocker and co-workers [5] while studying the reactions of aryl-methylated α-tetralones with selenium at 330-335° also observed the formation of dinaphthofurans,* to which they hypothetically assigned symmetrical structure. In the light of our results their hypothesis appears doubtful; it is quite probable that the compounds they obtained were unsymmetrical dinaphthofurans of type (II).

Being convinced that it was not possible to dehydrogenate α-tetralone (I) smoothly with selenium, we turned to another possible method of converting it into 1-naphthol—bromination and subsequent elimination of hydrogen bromide.



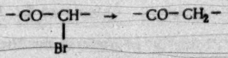
Bromination of α-tetralone proceeded quite smoothly [10, 11a], and we obtained an 82.5% yield of 2-bromo-1-keto-1,2,3,4-tetrahydronaphthalene (V). Elimination of hydrogen bromide from bromotetralone (V) turned out to be somewhat more complicated.

Thus, when bromotetralone (V) was heated with pyridine (130°, 5 hours), despite a complete cleavage of bromine, no 1-naphthol could be detected. This was explained by the formation of a quaternary pyridinium salt (VI), which we were able to isolate by carrying out the reaction in toluene.



(VI)

When we tried to eliminate hydrogen bromide by boiling the compound with diethylaniline, only a 30-39% yield (on the basis of α-tetralone) of 1-naphthol was obtained. Similarly low yields were obtained earlier with substituted bromotetralones ([5, 12, 13], but see [14]); this is evidently connected with a curious reaction in which α-bromoketones are reduced to ketones under the action of diethylaniline ([15], see also [16]).



$$-CO-\underset{\displaystyle Br}{\underset{|}{CH}}- \rightarrow -CO-CH_2-$$

We were able to increase the yield of 1-naphthol by replacing diethylaniline with triethylamine. Thus, when bromotetralone (V) was heated for 3 hours with an excess of triethylamine in trichlorobenzene solution in a 200° bath, we obtained a 75-76% yield (on the basis of bromotetralone (V) of 1-naphthol. By carrying out the conversion of α-tetralone into 1-naphthol without separating bromotetralone (V) we obtained a 64.5-66.5% yield (on the basis of α-tetralone) of 1-naphthol.

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*Their yields of substituted 1-naphthols were 3.6-12.5%.

We believe that the use of triethylamine with substituted bromotetralones and other ketones will make it possible to prepare corresponding aromatic hydroxy compounds in higher yields than was possible until now (for example see [5, 12, 13]).

On the basis of results obtained we were able to synthesize 1-naphthol-1-C^{14} in a 63.5% yield, counting from α-tetralone-1-C^{14}. In this case the reaction was carried out without separation of bromotetralone.

EXPERIMENTAL*

α-Tetralone was prepared by cyclization of γ-phenylbutyryl chloride [17]. The distilled product was thoroughly washed with a sodium carbonate solution and with water, then redistilled. It had a b. p. 115-116° at 8 mm, $n^{20}D$ 1.5691. According to lit. data [18], b. p. 105° at 3 mm, $n^{20}D$ 1.5691–1.5693.

Dehydrogenation of α-tetralone with selenium. We heated 2 g of α-tetralone with 1.08 g of granulated selenium (Shering-Kal'baum brand) for 10 hours in a flask linked through a ground joint to an air cooled condenser and placed in a 330 ± 2° bath.

We diluted the resulting dark, viscous mass with ether, decanted it from unreacted selenium (0.23 g, 21.3%), distilled off the ether, and after adding 10 ml of 10% sodium hydroxide we steam distilled the residue to remove neutral substances. When the distillate was extracted with ether and the ether evaporated, there remained 0.68 g of a colorless oil, which, after being boiled with 0.68 g of hydroxylamine hydrochloride and 0.68 g of potassium carbonate in dilute methanol, gave 0.51 g (23%) of α-tetraloxime. A recrystallization from methanol gave m. p. 102.5-103.5°. After removal of neutral substances, the residue in the flask was acidified with concentrated hydrochloric acid and again steam-distilled. From this distillate we extracted with ether 0.51 g (25.7%) of 1-naphthol, m. p. 93.5-95.5°.

The oil remaining in the distillation flask solidified on cooling into a black, glassy mass (weight 0.63 g). We triturated 0.35 g of it with 3 ml of methanol, filtered out the insoluble residue (filtrate a) and washed it with methanol; the yield was 0.12 g, m. p. 140-145°. After recrystallization from anhydrous alcohol we obtained colorless needles, m. p. 153.7-154.2°.

Found %: C 89.73, 89.63; H 4.70, 4.59. $C_{20}H_{12}O$. Calculated %: C 89.52; H 4.51.

Judging from the composition and melting point, the obtained compound was dinaphtho-(1',2':2,3; 1",2":4,5)-furan (II), for which the literature [4b] gives m. p. 155.0-156.5°. Addition of dinaphthofuran (IV) to this compound lowered the melting point to 126-130°.

We prepared a picrate and a 1,3,5-trinitrobenzene adduct of the synthesized dinaphthofuran (V).

Dipicrate gave orange needles, m. p. 162.5-163.5° (did not change after recrystallization from anhydrous alcohol).

Found %: N 11.65, 11.69. $C_{20}H_{12}O \cdot 2C_6H_3O_7N_3$. Calculated %: N 11.57.

A mixed sample with dipicrate of dinaphthofuran (IV) melted at 152-154°.

1,3,5-Trinitrobenzene adduct gave orange needles, m. p. 177.0-177.8° (after one recrystallization from benzene).

Found %: N 8.60, 8.79. $C_{20}H_{12}O \cdot C_6H_3O_6N_3$. Calculated %: N 8.73.

For dipicrate of dinaphtho-(1',2':2,3;1",2":4,5)-furan the literature gives [4b] m. p. 164.5-165.2°, for 1,3,5-trinitrobenzene (1:1) adduct – m. p. 178.2-179.2°.

After removal of dinaphthofuran (II), the methanol solution (filtrate a) was evaporated, the oily residue dissolved in 4 ml of ether, and the ether solution (b) was extracted with 5% sodium hydroxide. Acidification of alkaline solution gave 85 mg of a brown amorphous substance (c) which was readily soluble in ether, but insoluble in boiling alcohol and petroleum ether. Part of the substance was dissolved in ether for analysis, and the ether solution filtered and evaporated. The residue was kept for 24 hours over calcium chloride in a vacuum desiccator. The elementary composition of the substance turned out to be close to that of dihydroxydinaphthalene.

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*With the participation of I. S. Isaev and S. A. Kabanova.

Found %: C 83.51, 83.30; H 5.34, 5.35. $C_{20}H_{14}O_2$. Calculated %: C 83.85; H 4.92.

In alkaline solution the synthesized compounds underwent coupling with benzenediazonium chloride to give a red precipitate; when heated over a steam bath with acetic anhydride in pyridine, the compound gave an acetyl derivative which was not soluble in alkali and melted over a wide temperature range above 220°.

After extraction of substance (c), the ether solution was evaporated and the remaining light-yellow oil treated with 100 mg of picric acid in 2 ml of boiling anhydrous alcohol. When the alcohol cooled, 34 mg (0.7%) of dinaphthofuran (II) dipicrate precipitated, m. p. 148-154° (after several recrystallizations from anhydrous alcohol the melting point was raised to 159-160°). Total yield of dinaphtho-(1',2':2,3;1",2":4,5)-furan was 12.2%.

Reaction of 1-naphthol with selenium. Just as in the preceeding experiment we heated 2.0 g of 1-naphthol with 1.08 g of selenium for 10 hours in a 330 ± 2° bath. We triturated the viscous yellow green mass with 5 ml of ether, separated unreacted selenium (0.48 g, 44.5%), filtered off the ether-insoluble precipitate (a), and washed it with 20 ml of ether. From the ether filtrate we extracted with an alkaline solution 0.30 g (15%) of 1-naphthol, m. p. 78-90° (after steam distillation, m. p. 90-91°). We evaporated the remaining ether solution, and dissolved the yellow residue (0.77 g) together with precipitate (a) (0.41 g) in 10 ml of hot benzene; the resulting solution was filtered away from the sludge and evaporated down to 3 ml. Dinaphtho-(1',2':2,3;-2",1":4,5)-furan (IV) precipitated when the solution cooled; the yield was 0.58 g (31%), m. p. 172-177°, but after several recrystallizations from benzene–alcohol mixtures it gave colorless needles with a m. p. 182.0-183.3°. According to lit. data [20], m. p. 182-182.5°, 184°.

Found %: C 89.37, 89.49; H 4.64, 4.76. $C_{20}H_{12}O$. Calculated %: C 89.52; H 4.51.

Dipicrate of dinaphthofuran (IV) gave orange crystals with a m. p. 174-175°. According to lit. data [20], m. p. 171-173°.

Dinaphthofuran was also formed when the reaction was carried out at 300°.

Action of pyridine on 2-bromo-1-keto-1,2,3,4-tetrahydronaphthalene (V). Bromotetralone (V) was prepared by bromination of α-tetralone with an equimolar amount of bromine in absolute ether at 10° (see [11]); the yield was 82.5%, m. p. 37-39°. According to lit. data [21], m. p. 40-41°.

We heated 2.52 g of bromotetralone (V) and 1.64 g of pyridine for 5 hours in 15 ml of toluene in a 130° bath; a flask supplied with a reflux condenser was used. We filtered out the precipitate which formed, washed it with 3 ml of toluene and dried; the yield was 0.58 g, m. p. 213-217°. For purification we dissolved it in 6 ml of methanol and filtered; to the transparent solution we added ether till the appearance of turbidity and left standing, adding to it every hour (for two days) 0.2 ml of ether. From this we obtained pinkish crystals, m. p. 215-222.5° (decomp.).

Found %: C 59.60, 59.73; H 4.73, 4.82; N 4.79, 4.70. $C_{15}H_{14}ONBr$. Calculated %: C 59.21; H 4.64; N 4.61.

On the basis of analysis and melting point the obtained substance was N-(1-ketotetralyl-2)-pyridinium bromide (VI), for which the literature lists [22] m. p. 216-218° (decomp.).

We were unable to find any 1-naphthol among the reaction products.

Neither could we obtain any naphthol when we heated (under similar conditions) 0.5 g of bromotetralone with 10 ml of pyridine in the absence of a solvent, though all the bromine was cleaved and converted to Br^- ion (determined by potentiometric titration with silver nitrate).

Conversion of 2-bromo-1-keto-1,2,3,4-tetrahydronaphthalene (V) into 1-naphthol. 1) By the action of diethylaniline. We refluxed for 1 hour 20 ml of freshly distilled diethylaniline with a crude solution of bromotetralone (V) (made from 2 g of α-tetralone). Using 10% sodium hydroxide we extracted from the resulting dark brown solution 0.58 g (29.6% of α-tetralone converted) of 1-naphthol, m. p. 86.5-91.0°. In another experiment the yield was 39%.

2) By the action of triethylamine. We dissolved 0.5 g of bromotetralone (V) and 1 ml of triethylamine (b. p. 88-90°) in 5 ml of chlorobenzene on trichlorobenzene (b. p. 211-214°) and heated in a flask connected

to a reflux condenser through a ground joint. After the reaction mixture cooled, we added to it 10 ml of water (to dissolve triethylamine hydrobromide) and 20 ml of ether. The organic layer was separated, extracted with 10% sodium hydroxide, and the alkaline extract acidified to salt out 1-naphthol. The dependence of 1-naphthol yield on reaction conditions is shown in the Table.

Solvent	Reaction temperature	Length of heating (in hours)	Yield of 1-naphthol [computed on the basis bromotetralone (V) (in %)
C_6H_5Cl	100°	10	62.5
$C_6H_3Cl_3$	180	3	57.5
$C_6H_3Cl_3$	180	7	66.3
$C_6H_3Cl_3$	200	1	72.0
$C_6H_3Cl_3$	200	3	75.5 – 76.2 •

• M. p. 90.0-91.5°

Preparation of 1-naphthol-1-C^{14}. We used a previously described method [23] to prepare 1-keto-1,2,3,4-tetrahydronaphthalene-1-C^{14} from $NaC^{14}N$ (specific activity, 23.35 mC/mole). The yield was 91.5%, b. p. 114-118° at 8-9 mm.

We placed 103.3 mg of 1-keto-1,2,3,4-tetrahydronaphthalene-1-C^{14}, 887.3 mg of untagged 1-keto-1,2,3,4-tetrahydronaphthalene (6.78 mmoles in all), and 8 ml of absolute ether into a three necked flask which was supplied with a thermometer, a dropping funnel, and a stirrer (shaft was passed through the reflux condenser). While the solution was cooled with ice, we added 1.08 g (6.78 mmoles) of bromine with stirring, at such a rate as not to raise the temperature above 10°. Each drop of bromine was added only after the red color of a preceeding one had disappeared. The cooling bath was removed and after 1.5 hours the temperature increased to 20°. The colorless ether solution was transferred into a pear-shaped flask and the ether was distilled off. To the residue of 2-bromo-1-keto-1,2,3,4-tetrahydronaphthalene-1-C^{14} (yellow oil) we added 3 ml (21.7 mmoles) of triethylamine and 13 ml of trichlorobenzene (b. p. 211-214°). An air-cooled reflux condenser (300 mm long) at the top of which was sealed a water-cooled condenser (150 mm long) (to condense triethylamine vapors), was connected through a ground joint to the flask which was placed in a 200 ± 2° metal bath and kept at that temperature for 3 hours. We added 10 ml of water and 80 ml of ether to the resulting suspension; the ether layer was separated, washed twice with water, and extracted with 10% sodium hydroxide (once with 5 ml and 6 times with 1 ml portions). The dark-brown alkaline extract was filtered (without suction) through a layer of activated charcoal (10 mm in diameter, 5 mm high) which was subsequently washed with 2 ml of 10% sodium hydroxide. When the yellow colored alkaline solution was acidified, 1-naphthol-1-C^{14} precipitated. The yield was 0.62 g (63.5%), m. p. 90.5-92.5°, no halogen.

Activity was 2.33, 2.35 mC/mole • (see [23] for the method of measuring).

The literature [24] lists m. p. 94-96° for 1-naphthol. The grade of the product obtained by this method can be improved by increasing the thickness of the activated charcoal used to filter the alkaline solution, but it results in a lower yield.

SUMMARY

1. It was shown that, when α-tetralone was heated with selenium at 330° (10 hours), alongside dehydration to 1-naphthol (25.7% yield) a conversion of α-tetralone into unsymmetrical dinaphtho-(1',2':2,3;1",2":4,5)-furan took place (12.2% yield). 1-Naphthol under these conditions gave symmetrical dinaphtho-(1',2':2,3; 1",2":4,5)-furan (31% yield).

2. With triethylamine 2-bromo-1-keto-1,2,3,4-tetrahydronaphthalene eliminated hydrogen bromide to give 1-naphthol in a higher yield (75-76%) than with diethylaniline.

• The value calculated from the activity of initial $NaC^{14}N$ amounted to 2.43 mC/mole.

3. 1-Naphthol-1-C^{14} was synthesized in a 63.5% yield by starting from 1-keto-1,2,3,4-tetrahydronaphthalene-1-C^{14}.

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REACTIONS INVOLVING ORGANIC SOLIDS

XI. THE INFLUENCE OF TEMPERATURE ON THE CONVERSION OF N-ARYLAMIC ACIDS INTO IMIDES*

M. Kh. Gluzman

When amines react with cyclic anhydrides in organic solvents they give N-arylamic acids or corresponding imides. When the components are refluxed in chloroform [1-4], carbon tetrachloride [5], or benzene [1,6,7] one obtains N-arylamic acids, while in glacial acetic acid [8, 9] or, in isolated cases, in benzene [10] imides are formed. The latter are often prepared by treating N-arylamic acids with dehydrating agents: acetyl chloride [2, 11], acetic anhydride in the presence of sodium acetate [3, 12], phosphorus pentoxide [13], phosphorus oxychloride [14], phosphorus tri- and pentachloride and thionyl chloride [15]. Imides may also be formed by fusion of amines with acids [16, 17] or anhydrides [18, 19], by heating N-arylamic acids above their melting points [2, 3, 20-23], or by boiling aqueous suspensions of amines and anhydrides [24].

All the authors who converted N-arylamic acids into imides by heating the acids above their melting points ignored the question of temperature and duration of heating. Only Alexander and McElvain [5] picked 145° and a time of 30 minutes for the cyclization of N-aryl-3-nitrophthalamic acids, but they did not bring up the question of degree of imidation either. It is quite obvious, that these conditions could not be general for all N-aryl-3-nitrophthalamic acids regardless of their structures and melting points.

We have worked out a method of preparing N-arylamic acids from solid amines and solid anhydrides [25]. By studying this reaction through comparison of heating curves [26] and the kinetics of amine acylation involving solids [27, 28], we were able to work out the conditions which would guarantee quantitative yields of N-arylamic acids and were able to explain what fraction of liquid [29] and gaseous [30] phases participated in these processes. From the kinetic data and heating curves one could form an opinion about the effect of temperature and length of heating on the degree of conversion of N-arylamic acids to imides. Moreover, full knowledge of the effect of these factors on the process of imide formation is essential for the solution of many problems (in particular, in construction of amine—anhydride phase diagrams [31] and in design of commercial methods of acylating amines in the solid phase [32] and can only be acquired through kinetic studies at different temperatures. Kinetic data can also be utilized to work out methods of preparing imides by heating N-arylamic acids in the solid phase, or at least, at possibly lower temperatures.

In connection with this we studied the kinetics of N-arylamic acid conversion to imides at various temperatures. The results of these studies on six N-arylamic acids are given in the Table, while the course of imide formation with time is drawn in Figs. 1-5.

From these data we could make the following deductions.

1. Conversion of N-arylamic acids into corresponding imides depends primarily on the nature of the compounds. The first five N-arylamic acids (see the Table) do not have significantly different melting points, but at approximately similar temperatures they cyclize at completely different rates. While 4-nitrophenylmaleamic acid is almost completely converted into imide in 2.5 hrs. at 160° (Fig. 1), p-tolylmaleamic acid (Fig. 2) and β-naphthylmaleamic acid (Fig. 3) give almost 80% conversion, whereas p-chlorophenylmaleamic

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* See J. Phys. Chem. 32, 388 (1958) for the preceding communication.

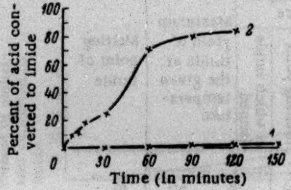


Fig. 1. Conversion of N-(4-nitrophenyl)-maleamic acid to the imide.
1) At 160°; 2) at 180°.

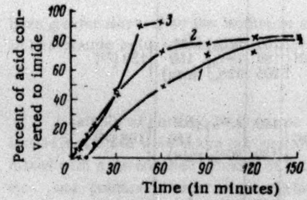


Fig. 2. Conversion of N-(p-tolyl)-maleamic acid to the imide.
1) At 160°; 2) at 180°; 3) at 205°.

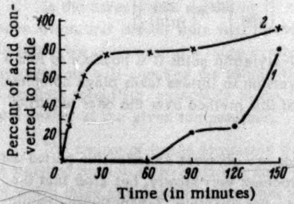


Fig. 3. Conversion of N-(2-naphthyl)-maleamic acid to the imide.
1) At 160°; 2) at 180°.

acid is already quantitatively converted to the imide in 40 minutes at 143° (Fig. 4, isotherm II).

At temperatures below melting, p-carboxyphenylmaleamic acid remains entirely in the form of acid, and even if kept at the melting point for 100 minutes it yields only about 7% of imide (Fig. 4, isotherm I), while phthalazol already begins to change into imide at 125°, i.e., 140° below its melting point (Fig. 5).

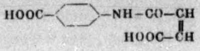
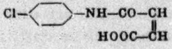
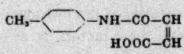
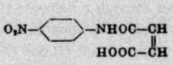
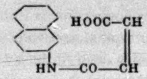
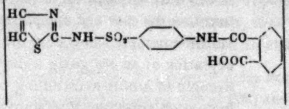
Since none of the investigated compounds have bulky groups which could hinder the approach of a carboxyl to the amide group, then the degree of conversion to an imide apparently depend only on the electron affinities of the substituents in the benzene ring. Imide formation is nothing else but an intramolecular acylation of an imine group by a carboxyl, and two things are necessary for the elimination of water: spatial proximity between an NH- and COOH group and a sufficient mobility of the hydrogen in the imino- and hydroxyl groups. Both these factors, or at least the second, are undoubtedly determined by the nature of substituents which transmit their effect through a benzene ring. With this in mind, it becomes immediately apparent (see the Table), that out of the first four arylamic acids (I) and (IV), which have strong negative substituents (COOH- and NO_2^- groups) para to the NH group, give poor conversion to imides, while acids (II) and (III), which contain typical substituents of the first kind in a para position, cyclize readily even in the solid phase (40° below their melting points). In this case the same factor appears, the effect of which determines the rate and completeness of acylation in primary amines—namely, their base strength; the rate and degree of acylation of an NH group is directly proportional to the base strength of amine constituting the N-arylamic acid. The base ionization constants of p-aminobenzoic acid, p-chloroaniline, p-toluidine, and p-nitroaniline at 25° are: $2.8 \cdot 10^{-12}$, $1.5 \cdot 10^{-10}$, $2 \cdot 10^{-9}$, and $4 \cdot 10^{-12}$ respectively.

The fact, that nitro and carboxyl groups on the one hand, and methyl groups and chlorine on the other, retain the same effects on imino groups as on unacylated amines points to the predominant effect of these substituents in comparison to the effect of introduced acyl radicals.

The same effects govern the rate and degree of imide formation from β-naphthylmaleamic acid and phthalazol. Imide formation proceeds readily, since the base ionization constants of β-naphthylamine and nor-sulfazol are of the order of 10^{-12} and 10^{-9}.

In the light of these ideas there seems to be completely no justification for the attempts of Alexander and McElvain to convert N-aryl-3-nitrophthalamic acid into imide in half an hour at 145° without considering the nature of the amine, which plays the dominant role in the cyclization process.

2. It is possible to find for each N-arylamic acid a temperature threshold below which no conversion to imide occurs. As our studies have shown [26-28], in many cases this threshold lies above the temperatures needed to produce quantitative yields of monoamides. But if imide formation proceeds alongside monoacylation, then after completion of reaction one has to open the imide ring under milder conditions so as not to saponify the amide bond too.

Compound No.	Name of N-arylamic acid	Formula	Temperature: melting point	Temperature: at which imide formed	Maximum yield of imide at the given temperature	Melting point of imide
I	N-(4-Carboxyphenyl)-maleamic acid		214°	214°	7% (for 100 min)	
II	N-(p-Chlorophenyl)-maleamic acid		185	143	96% (for 40 min)	145°
III	N-(p-Tolyl)-maleamic acid		201	160 180 205	76% 78% 92% (for 150 min)	150 [33]
IV	N-(p-Nitrophenyl)-maleamic acid		207	160 180	2.5% 80% (for 150 min)	168 [33]
V	N-(2-Naphthyl)-maleamic acid		200	160 180	77% 93% (for 150 min)	128
VI	Phthalazol		267	130 140 150	6% 24% (for 360 min) 33% (for 330 min)	274

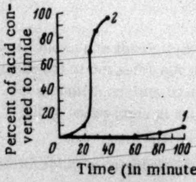


Fig. 4. Conversion of N-(aryl)-maleamic acids to the imides. 1) N-(4-Carboxyphenyl)-maleamic acid at 214°; 2) N-(p-chlorophenyl)-maleamic acid at 143°.

On the other hand, for many N-arylamic acids it is possible to find a temperature range within which conversion to imides takes place completely in the solid phase. The advantages of this method over the ones requiring condensing agents are quite obvious.

3. With some N-arylamic acids one observes an induction period during which the conversion to imide proceeds very slowly, but after that the reaction erupts at a much higher rate. For example, 2-naphthylmaleamic acid does not undergo cyclization during the first hour at 160°, but soon after that the rate of imide formation rapidly increases and in 1.5 hours about 80% of the imide is formed (Fig. 3). p-Chlorobenzene gives only 5-6% of imide during the first 40 minutes of heating in the solid state at 143°, but after that, the reaction goes to completion in 5-10 minutes (Fig. 4). α-Naphthyltetrachlorophthalamic acid has an induction period of over 3 hours, after which the imide formation proceeds at a high rate. Such a behavior is typical of autocatalytic reactions. In this case the water eliminated in the process or the forming imide could have a catalytic effect on the reaction.

4. The rate and degree of imide formation are a function of temperature and time, but they depend more on the temperature. The curves in Fig. 6, which gives the degree of imide formation in phthalazol as a function of temperature within the same time intervals, show that at temperatures very far removed from the melting point of phthalazol (~269°) the curves giving imide formation in the solid phase as a function of temperature

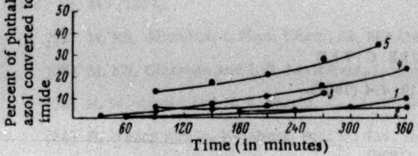


Fig. 5. Conversion of phthalazol to the corresponding imide under isothermal conditions.
1) At 125°; 2) at 130°; 3) at 135°; 4) at 140°; 5) at 150°.

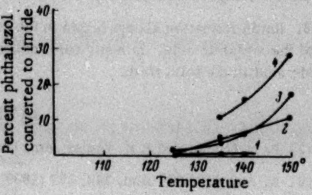


Fig. 6. The course of phthalazol conversion to the imide as a function of temperature.
1) During 30 minutes; 2) during 90 minutes; 3) during 150 minutes; 4) during 270 minutes.

have greater slopes than the isotherms at those same temperatures. An even greater difference can be observed in N-arylamic acids whose isotherms are shown in Figs. 1 and 3.

EXPERIMENTAL

A sample of purified N-arylamic acid was placed in an oil constant-temperature bath, and at fixed time intervals samples were taken out and analyzed for N-arylamic acid. A weighed portion of ground sample was mixed with a determined amount of 0.1 N NaOH in cold, and the excess alkali was titrated to the phenolphthalein end point. In order to ascertain that the undissolved (in 0.1 N NaOH) part of the sample was the imide and not diamide or a resin, we filtered it out, washed with water, dried at 60-80° to a constant weight, and heated with an alkaline solution of such a concentration as would only open an imide ring without involving an amide linkage. The conditions were chosen beforehand for each imide. Certain imides were readily converted to N-arylamic acids when treated with 2% NaOH in cold [33]; with others the ring could be opened by heating in 5% NaOH at 40-80°.

In the cases where according to analytical results almost no imide formation took place misgivings might have arisen that imides were still formed but were readily cleaved in the process of titration with 0.1 N NaOH in cold. We investigated a large number of imides without encountering any such easy cleavage of imide rings; however, we still checked the solubilities of investigated samples in sodium carbonate and bicarbonate solutions. Complete solubility, especially in the latter, assured us that no ring closure took place when N-arylamic acid was heated at the given temperature.

The course of imide formation was also checked by the quantity of water given off in the cyclization. A weighed portion of N-arylamic acid was placed in a vessel which had a stopper with a tube at the other end of which three calcium chloride tubes were attached in series. After a fixed time of heating in a constant temperature bath, the water drops which condensed inside the tube were distilled into the calcium chloride absorbers and these were then weighed on an analytical balance.

The imides obtained were treated in cold or with slight heating with a 5% sodium carbonate solution (to wash away N-arylamic acid) the precipitates were washed with water till it gave a neutral reaction, and dried at 60-80°. After that, they were recrystallized from organic solvents, best of all from a chloroform – petroleum ether (1 : 1) mixture. The melting points of purified imides were checked against the ones given in the literature, but in cases where these were not found in the literature, the melting points were compared with those of imides prepared according to Wanag [34]. p-Carboxyphenylmaleimide was not isolated, since it was formed in very small amounts, and it was impossible to separate it from p-carboxyphenylmaleamic acid by dissolving only the latter in a carbonate solution – the presence of a carboxyl group in the imide made it soluble too.

SUMMARY

1. We studied the conversion of N-arylamic acids to the corresponding imides in the course of heating them at various temperatures.

2. We showed that the rate and degree of imide formation depended on the structure of N-arylamic acids and the base strength of the primary amines from which they were formed.

3. Imide formation always began in the solid phase, sometimes at temperatures far below the melting point of the arylamic acid. In many cases complete conversion to imide could be achieved by heating the arylamic acid in the solid state.

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CYCLOALKYLATION OF PHENOLS AND THEIR ETHERS

I. CONDENSATION OF PHENOL WITH CYCLOHEXANOL

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Cyclohexylphenol was first prepared by N. Kursanov [1] through diazotization of p-aminocyclohexylbenzene.

Wuyts [2] prepared p-cyclohexylphenol by direct alkylation of phenol with cyclohexanol in the presence of p-toluenesulfonic acid.

Schrauth and Görig [3], and later Bartlett and Garland [4], by using phosphorus pentoxide as the condensing agent, prepared a mixture of o- and p-cyclohexylphenol in a 75% yield. Besides these condensing agents, H_2SO_4 [4, 5], $ZnCl_2$ [4-6], or $ZnCl_2$ in HCl solution [5] have also been used in the alkylation of phenol with cyclohexanol. Phenol and its ethers have also been alkylated with cyclohexene and cyclohexyl chloride in the presence of H_2SO_4 [7], $AlCl_3$ [8], $ZnCl_2$ [8], BF_3 [9], and $BF_3 \cdot H_3PO_4$ [10]. The yields of cycloalkylation products range from 15 to 60%. p-Cyclohexylphenol can also be formed in the isomerization of cyclohexyl phenyl ether in the presence of fuming hydrochloric acid [11].

In the course of the work going on in our laboratory on the alkylation of aromatic rings with alcohols we studied the condensation of phenol with cyclohexanol in the presence of $AlCl_3$ and H_3PO_4 [12]. By carrying out a comparative study of the different modifications of alkylation we aimed at explaining the effect of catalysts and reaction conditions on the yields and compositions of products. The condensation of phenol with cyclohexanol in the presence of $AlCl_3$ was at first carried out in the usual way. To a phenol–cyclohexanol mixture we added at room temperature and in small portions $AlCl_3$ (0.5-2 moles per 1 mole of cyclohexanol), then heated the mixture (3-7 hours). When the reagents were used in equimolar amounts the yield of products was small (27-30%). An increase in the amount of aluminum chloride to 2 moles or a raised temperature had little effect on the total yield of products (Table 1, Series I), but was accompanied by a larger amount of high boiling products. The main product in these reactions was p-cyclohexylphenol. Very small amounts of cyclohexyl phenyl ether or o-cyclohexylphenol were formed. When these experiments were carried out with excess of phenol (up to 5 moles), then it was enough to use 1 mole of $AlCl_3$ in order to obtain a good yield of cyclohexylphenols (Table 1, Series II). It was possible to increase the yield to 60% by keeping the amounts of reagents constant and changing the reaction temperature from 20 to 90-100°. The optimum conditions for such condensations were to heat the reaction mixture for 3 hours at 70-80°.

In contrast to the preceeding series of experiments, the ones with excess of phenol gave a mixture consisting of almost equal amounts of o- and p-cyclohexylphenols. Besides these we detected cyclohexyl phenyl ether, which upon distillation isomerized completely to the ortho isomer.

In both variations of the condensation we discovered among the reaction products cyclohexyl chloride, the quantity of which increased with decrease in temperature.

Further on, we carried out a series of condensations with aluminum phenoxychloride prepared beforehand. Phenol was used in excess (3-5 moles), and the quantity of aluminum chloride was varied from 0.28 to 1.5 moles per mole of cyclohexanol. The reaction temperature was varied from 50 to 130°. Aluminum chloride was added in small portions to the melted phenol (at 90-100°). After that, cyclohexanol was added through a dropping funnel to the prepared aluminum phenoxychloride. The yield of reaction products was about 64%

TABLE 1

Condensation of Phenol with Cyclohexanol• in the Presence of $AlCl_3$

Molar ratios of phenol : : cyclohexanol: $AlCl_3$	Temperature	Reaction time (in hours)	Yield of products (in %)			High-boiling residue (in g)
			cyclohexyl phenyl ether	o-cyclohexylphenol	p-cyclohexylphenol	
			I Series			
1 : 1 : 1	18–20°	96	5.7	4.0	18.0	3.2
1 : 1 : 1	50–60	3	4.0	5.7	20.4	3.7
1 : 1 : 1	90–95	7	2.2	4.5	11.4	10.6
1 : 1 : 1.5	18–20	24	4.0	—	29.4	4.2
1 : 1 : 2.0	90–95	6	—	—	20.0	3.5
			II Series			
5 : 1 : 1	25–30	6	—	17.6	35.7	1.35
5 : 1 : 1	50–60	3	8.5	23.3	21.0	—
5 : 1 : 1	70–80	3	8.5	28.4	24.0	—
5 : 1 : 1	90–100	3	9.5	17.0	31.7	—
			III Series (by formation of $C_6H_5OAlCl_2$)			
5 : 1 : 1	50	11.0	8.5	19.0	20.0	—
5 : 1 : 1	90	6.5	7.0	22.6	18.0	—
5 : 1 : 1	50–130	7.0	11.0	13.0	34.0	—
5 : 1 : 1	120–130	2.5	22.6	13.0	22.6	—
5 : 1 : 1	120–150	5.0	24.0	15.5	24.0	—

•In all these experiments the amount of cyclohexanol was 10 g (0.1 moles).

(Table 1, Series III). The reaction products were: o- and p-cyclohexylphenol and cyclohexyl phenyl ether; no cyclohexyl chloride was detected. In these experiments the amounts of cyclohexyl phenyl ether were appreciable, attaining 24% in some cases. However, we were unable to isolate this ether in a pure form, since it isomerized completely to o-cyclohexylphenol during distillation.

Thus in these experiments the yield of o-cyclohexylphenol exceeded that of the para isomer. The absence of cyclohexyl chloride and the formation of comparatively large amounts of ether fraction prompted us to assume that in these condensations cyclohexyl phenyl ether was the principal intermediate product as well as being the source of the ortho isomer.

$$C_6H_5OH + AlCl_3 \longrightarrow C_6H_5OAlCl_2 \xrightarrow{C_6H_{11}OH}$$

$$\longrightarrow \underset{\searrow o\text{-}C_6H_{11}C_6H_4OH}{C_6H_5OC_6H_{11}} + n\text{-}C_6H_{11}C_6H_4OH + o\text{-}C_6H_{11}C_6H_4OH$$

The investigations on phosphoric acid as a condensing agent for the alkylation of phenols with alcohols are described in the works of Chichibabin [13], Tambovtseva and Tsukervanik [14], Sudorova [15], and in a series of patents. These indicate the advantage of these reactions—high yields of pure, easily separated products. According to Chichibabin's data [13], ortho-alkylphenols are obtained with phosphoric acid. However, all the subsequent works indicate that only p-alkylphenols are obtained.

Hart and Hagland [16] prepared p-tert-butyl-o-cresol (63%) by alkylating o-cresol with tert-butyl alcohol. They separated the reaction products by treating the mixture with 10% NaOH. When we succeeded in working out a better method of separating o- and p-alkylphenols, we again repeated the condensation of phenol with cyclohexanol in the presence of phosphoric acid. We carried out the reaction by adding cyclohexanol gradually to a mixture of phenol (1 mole) and phosphoric acid (d 1.86, 3 moles). The reaction mixture was heated at 50-130°. The yield of monocyclohexylphenols was 80%.

TABLE 2

Condensation of Phenol with Cyclohexanol * in the Presence of H_3PO_4

Molar ratios of phenol : : cyclohexanol : H_3PO_4	Temperature	Reaction time (in hours)	Yields of products			High-boiling residue (in g)
			Cyclohexyl phenyl ether	o-cyclohexylphenol	p-cyclohexylphenol	
1 : 1 : 3	50—60°	3.5	29.0	4.5	25.5	2.6
1 : 1 : 3	70—85	3.0	25.5	13.0	41.0	—
1 : 1 : 3	90—95	3.0	16.0	24.0	34.6	—
1 : 1 : 3	120—130	3.0	11.0	25.0	41.0	—

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* In all the experiments the quantity of cyclohexanol was 10 g (0.1 moles).

Contrary to our previous data [12], there was an appreciable amount of o-cyclohexylphenol among the reaction products. Cyclohexyl phenyl ether, which was also formed in appreciable amounts, would partially or completely isomerize to o-cyclohexylphenol during distillation. Thus we obtained almost the same quantity of ortho as of para isomer (Table 2). One can judge the isomeric composition of alkylphenols only on the basis of separated pure individual products. The usual treatment of reaction products with 10% sodium hydroide did not separate out the alkylphenols completely. Only through a repeated treatment of the crude reaction mixture with 20% alkali were we able to separate the ortho and p-cyclohexylphenols from other products. We separated the isomers from each other by taking advantage of the difference in solubilities of their sodium salts in alkaline solutions.

EXPERIMENTAL

The reaction was carried out in a three-necked flask to which was attached a reflux condenser, a mechanical stirrer, and a thermometer (sometimes a dropping funnel). In Table 1 and 2 we have shown examples of typical reactions.

I. We added $AlCl_3$ over a period of 0.5-2 hours to a phenol—cyclohexanol mixture in a solvent or in excess phenol. The mixture was either left at room temperature over varying lengths of time, then heated, or heated right away. When evolution of HCl ceased, the mixture was cooled, decomposed with weakly acidic water, and extracted with benzene. The benzene solution was repeatedly treated with 20% sodium hydroxide. During this treatment the p-cyclohexylphenolate precipitated as a crystalline mass,* while phenolates of ortho isomer and of unreacted phenol remained in the alkaline solution. The benzene solution contained ethers and polycyclohexylphenols. The solid phenolate of para isomer was separated and washed several times with benzene. The extract was added to the main benzene solution. Decomposition of the solid phenolate with dilute hydrochloric acid solution gave crude p-cyclohexylphenol, m. p. 120-124°. The alkaline solution of phenolates was extracted with benzene or ether after decomposition with hydrochloric acid. The extract was washed with water and dried, then the solvent was distilled off. Fractionation in vacuum yielded o-cyclohexylphenol, b. p. 115-118° (at 2 mm), a colorless, oily, crystallizable liquid, m. p. 49-52°. The benzene solution was washed with water, dried, and fractionated. The following fractions were collected during vacuum distillation: 1st, b. p. 118-160° (at 2 mm), mixture of ethers; 2nd, b. p. 160-200° (at 2 mm), viscous yellow mass which would not crystallize and turned out to be a mixture of polycyclohexylphenols and their ethers.

When an excess of phenol was used in these experiments, the polycyclohexylphenol fraction was absent and the ether fraction gave on distillation (b. p. 118-120° at 2mm) an oily liquid, from which o-cyclohexylphenol (m. p. 53-54°) crystallized.

II. To the melted phenol at 40-100° we added aluminum chloride in small portions. As it was being added hydrogen chloride was evolved. After the evolution of HCl ceased, we added (still at 40-100°) cyclohexanol over a period of 1-1.5 hours. Each drop of added cyclohexanol caused a renewed evolution of HCl.

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* If the insoluble phenolate did not precipitate immediately, then the mixture was left standing for several hours.

As more and more cyclohexanol was added the reaction mixture changed in color from pink to raspberry black. After addition of alcohol was completed, the reaction mixture was heated for another 1-10 hours at the same temperature and left till the next day. Further treatment and separation of reaction products were carried out in the same way as described above. In this case the isolated products were purer; decomposition of phenolates gave a para isomer with m. p. 124-125° and an ortho isomer with b. p. 124-125° (at 5 mm), m. p. 52-53°. During distillation the ether fraction isomerized completely into the ortho isomer, which had the same constants as the one above.

III. To a mixture of phenol and phosphoric acid we added (at 50-130°) cyclohexanol through a dropping funnel over a period of 1-1.5 hours. As more and more cyclohexanol was added the color of the reaction mixture gradually changed from pale pink to raspberry black. After that, the reaction mixture was heated at the same temperature and left till the next day. On standing, the reaction mixture separated into two layers : semisolid on top, liquid mass below. The reaction mixture was diluted with water, extracted with benzene, and treated as described before. Distillation of the ether fraction gave two fractions: 1st, b. p. 103-108° (at 3 mm), 114-120° (at 4 mm), was a white pleasant-smelling labile liquid; 2nd, b. p. 112-118° (at 3 mm), 125-130° (at 4 mm), was a slightly yellowish viscous liquid which crystallized (m. p. 55-56°) on standing or seeding with the ortho isomer. A second distillation of the first fraction gave cyclohexyl phenyl ether.

B. p. 90-91° (at 2 mm), d^{20}_4 1.005, $n^{20}D$ 1.5250, MR_D 53.62; calc. 53.44.

To identify the condensation products we combined the corresponding fractions of all the experiments (different modifications) and redistilled or recrystallized them again. From this we obtained much purer products which were characterized by their respective constants.

p-Cyclohexylphenol [3] – white needle-like crystals, b. p. 134-135° (at 4 mm), m. p. 130° (from benzene).

2,6-Dinitrocyclohexylphenol [4] was prepared by treating p-cyclohexylphenol with nitric acid (d 1.4) in glacial acetic acid. It formed light-yellow leaflets, m. p. 84-85° (from ethyl alcohol).

p-Cyclohexylphenoxyacetic acid, m. p. 151° [17]; benzyl ether, m. p. 117-118° [5]; acetate, m. p. 35-36° [18]; methyl ether, m. p. 55-56° [8]; ethyl ether, m. p. 40° [8]; phenylurethane, m. p. 144-145°.

o-Cyclohexylphenol [3] – colorless oily liquid, b. p. 124-125° (at 5 mm), m. p. 56° (from petroleum ether).

4,6-Dinitrocyclohexylphenol [4]. We dissolved 10 g of o-cyclohexylphenol in 30 ml of glacial acetic acid. To the mixture we added at 15-20° and with vigorous stirring 30-35 ml of nitric acid (d 1.4 or 1.34) over a period of 3 hours. After that, the mixture was left standing at room temperature till the next day. After the usual treatment we obtained 12.6 g (85%) of the dinitro derivative, m. p. 105-106° (from ethyl alcohol). Dinitro-o-cyclohexylphenol (DINOPH) is used to protect plants against diseases and pests [19]. Our compound was tested against a pest in the cotton plant and was found to be very effective.

o-Cyclohexylphenoxyacetic acid, m. p. 129-131°; benzyl ether, m. p. 39° [9]; methyl ether [8], b. p. 101-103° (at 2 mm), d^{20}_4 1.0111, $n^{20}D$ 1.5345, MR_D 58.54; calc. 58.07; ethyl ether [8], b. p. 114-115° (at 3 mm), d^{20}_4 0.9991, $n^{20}D$ 1.5270, MR_D 62.77; calc. 62.69.

SUMMARY

1. Condensations between cyclohexanol and phenol in the presence of aluminum chloride were investigated. Depending on the conditions of condensation and the amounts of reagents one obtained different quantities of ortho and p-cyclohexylphenols and of cyclohexyl phenyl ether. The total yield of the above named compounds was as high as 60%.

2. Contrary to previous data, it was shown that in the presence of phosphoric acid the reaction products contained appreciable quantities (up to 50%) of o-cyclohexylphenol. The total yield of cyclohexylphenols attained 80%.

3. In all these cases, cyclohexyl phenyl ether was partially or completely isomerized during distillation to o-cyclohexylphenol.

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* Original Russian pagination. See C. B. Translation.

** In Russian.

MERCAPTOAMINES

I. β-MERCAPTOETHYLAMINE AND ITS N-SUBSTITUTED DERIVATIVES

F. Iu. Rachinskii, N. M. Slavachevskaia and D. V. Ioffe

Due to their pharmacological [1-3] and chemical [4, 5] properties β-mercaptoethylamine and its derivatives have recently attracted the attention of more and more investigators. However, the synthesis and properties of these compounds are not sufficiently well covered in the literature, which fact prompted us to carry out the present investigation.

β-Mercaptoethylamine was first prepared by Gabriel [6] by the acid cleavage of N-(β-mercaptoethyl)-phthalimide. Later he used for this purpose the reaction between ethylenimine and hydrogen sulfide [7] and also acid cleavage of 2-mercaptothiazoline [8], obtained from the reaction of carbon disulfide with β-bromoethylamine [9] or ethanolamine [10]. Besides this, β-mercaptoethylamine can be prepared by the reaction of β-chloroethylamine with potassium hydrogen sulfide and by alkaline saponification of S-β-aminoethylisothiourea hydrochloride.

An experimental investigation of different methods of preparing β-mercaptoethylamine (carried out under the direction of I. S. Ioffe) led us to the conclusion that the two most rational methods were: reaction of ethylenimine with hydrogen sulfide (as modified by Bestian [11]) and acid cleavage of 2-mercaptothiazoline, obtained directly from ethanolamine.

Unlike Knorr [10], we prepared 2-mercaptothiazoline in an aqueous medium in the presence of an emulsifier, and consequently the yield of 2-mercaptothiazoline was raised to 85% (computed from ethanolamine).

The acid clearing of 2-mercaptothiazoline was accomplished by refluxing the compound for a long time with concentrated hydrochloric acid. The β-mercaptoethylamine hydrochloride obtained from this contained up to 5% of bis-(β-aminoethyl)-disulfide.

β-Mercaptoethylamine was a strong base and readily formed various salts (Table 1).

The β-mercaptoethylamine base ionization constant was determined from the half-neutralization point on a potentiometric titration curve and turned out to be $4.8 \cdot 10^{-6}$ at 18°, only about one order of magnitude smaller than the base constant of monoethanolamine ($K = 3.1 \cdot 10^{-5}$). Air oxygen and weak oxidizing agents readily oxidized β-mercaptoethylamine in alkaline solutions to the disulfide. Oxidation was catalyzed by divalent ions of copper and iron. Under the action of strong oxidizing agents (hydrogen peroxide in acetic acid) it formed taurine (aminoethylsulfonic acid). The free base as well as the hydrochloride of β-mercaptoethylamine readily condensed with carbonyl compounds to form thiazolidines and mercaptals [12, 14].

N-Substituted β-mercaptoethylamines can be prepared by reacting corresponding N-substituted β-haloethylamines with potassium hydrogen sulfide and by hydrolytic cleavage of isothiourea compounds [13]. In both cases the amino alcohols (starting materials) are not readily available. A more expedient method is to synthesize the N-substituted β-mercaptoethylamines by the condensation reaction between ethylene sulfide and amines. Ethylene sulfide is relatively easily prepared by reacting ethylene oxide with thiourea in xylene; the yield is about 70% (calculated from thiourea). Despite the fact that the condensation between sulfides and amines is sufficiently well covered in the literature [15-19], the optimum conditions for the reaction are not yet established. We found out that one should distinguish two cases of the ethylene sulfide reaction with amines: reactions with strongly basic and weakly basic amines. While strongly basic amines (for example dimethylamine)

TABLE 1

Properties of Some β-Mercaptoethylamine Salts

Salt	Melting point	%SH	
		calculated	found
Hydrochloride	70°	29.1	28.6
Hydrobromide	159 – 160	20.8	20.9
Ascorbinate	90	12.9	13
Nicotinate	132 – 134	16.3	16.5
Salicylate	104 – 105	15.3	15.3

react readily with ethylene sulfide in cold in the presence of nonprotonic solvents (anhydrous benzene), weakly basic amines (for example aniline and its derivatives) react with ethylene sulfide slowly. In the case of weakly basic amines the reaction is facilitated by the use of enolizable solvents (alcohols) and by heating. If the reaction between strongly basic amines and ethylene sulfide is carried out in alcohol, an extensive polymerization of the latter takes place, and the yield of mercaptoamines is sharply reduced [17]. Amines with small base ionization constants (ethyl p-aminobenzoate, o- and p-nitroanilines) do not react with the sulfide under the above described conditions. But (as Iu. K. Iur'ev's investigations [19] have shown) this reaction can be accomplished through heating in sealed tubes.

Table 2 lists the properties of synthesized N-substituted β-mercaptoethylamines. The base ionization constants of N-alkylsubstituted β-mercaptoethylamines, in contrast to those of the N-arylsubstituted ones, are close to the constants of β-mercaptoethylamine itself. N-substituted β-mercaptoethylamines are comparatively stable toward weak oxidizing agents, yet in the presence of divalent iron ions they will be oxidized by oxygen in the air to corresponding disulfide.

Besides the ones obtained from oxidation of mercaptoamines the disulfides were also prepared (60-85% yield) by reacting corresponding β-haloalkylamines with sodium disulfide in aqueous solution. With the exception of bis-(β-aminoethyl)-disulfide, the disulfides were sparingly soluble in water but highly soluble in organic solvents. Table 3 lists the properties of synthesized aminodisulfides.

EXPERIMENTAL

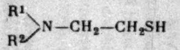
2-Mercaptothiazoline. We added 61 g of monoethanolamine and 0.3 g of an emulsifier (OP-10) to an aqueous sodium hydroxide solution (120 g in 180 ml of water) cooled to 0°. To the cooled mixture we added 120 g of carbon disulfide with vigorous stirring and heated the mixture for 6 hours at 40-50°. After that, the reaction mixture was heated for 4 hours at 100°. After the solution cooled, a crystalline product was filtered out and washed with glacial acetic acid. The m. p. 106° (from water). The yield 101 g (85%).

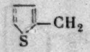
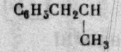
β-Mercaptoethylamine hydrochloride. We refluxed 300 g of 2-mercaptothiazoline in 600 ml of concentrated hydrochloric acid for 72 hours. Cooled solution was diluted with water, the unreacted 2-mercaptothiazoline removed, the filtrate treated with charcoal and evaporated. The viscous mass (residue) was kept for several days in a vacuum desiccator over solid potassium hydroxide. The m. p. was 70°. The yield 244 g (96%). The salts of β-mercaptoethylamine were prepared by reacting β-mercaptoethylamine bases with equivalent amounts of respective acids in aqueous solutions; water was subsequently distilled off in vacuum.

Bis-(β-aminoethyl)-disulfide. A current of carbon dioxide-free air was bubbled through a solution of β-mercaptoethylamine (77 g) in ethyl alcohol (400 ml) which also contained 5 ml of a 0.1 N ferrous sulfate solution. After 6 hours the reaction was over; this was determined by the negative test for a mercapto group. The solution was treated with charcoal, filtered, and the filtrate saturated with dry hydrogen chloride. The resulting precipitate was filtrated out and washed with acetone. When the alcoholic filtrate was concentrated and treated with an equal volume of acetone, additional disulfide precipitated. The m. p. was 212° (from alcohol). Yield 101.5 g (90%).

Other disulfides were prepared under similar conditions (Table 3).

TABLE 2

Properties of N-Substituted β-Mercaptoethylamines 
$$\genfrac{}{}{0pt}{}{R^1}{R^2}\!\!>\!N-CH_2-CH_2SH$$

Compound No.	R¹	R²	Boiling point (pressure in mm)	d_4^{20}	n_D^{20}	MR_D **		Molecular weight ***		K_a (17 ± 1°)	Melting point of hydrochloride
						calculated	found	calculated	found		
1	CH_3	CH_3	120—127°	0.8987	1.4675	32.3	32.45	105	108.5	69 · 10^{-7}	156—157°
2	C_2H_5	C_2H_5	160—162	—	1.4670	41.53	—	133	138	5.6 · 10^{-7}	172—173
3 *	n-C_3H_7	n-C_3H_7	109—110 (3)	0.8434	1.4502	50.77	51.32	161	176	4.3 · 10^{-6}	
4 *	iso-C_3H_7	iso-C_3H_7	125—126 (16)	0.8644	1.4503	50.77	51.30	161	164	2.7 · 10^{-6}	
5.	n-C_4H_9	n-C_4H_9	135 (10)	0.8664	1.4635	60.01	60.25	189	187	—	112—113
6 *	iso-C_4H_9	iso-C_4H_9	160—179	0.8664	1.4678	60.01	60.62	189	177	1.7 · 10^{-6}	
7 *	$C_6H_5CH_2$	$C_6H_5CH_2$	196—198 (2)	1.0472	1.5760	80.43	81.20	257	240	2.4 · 10^{-8}	
8 *	$C_6H_5CH_2CH_2$	H	107—110 (2)	1.0395	1.5540	55.89	55.80	181	176	1.3 · 10^{-6}	
9 *	C_6H_{11}	H	152—157 (4)	1.0760	1.5448	48.57	46.82	159	161	—	
10 *		H	138—140 (6)	1.1514	1.5776	50.37	49.83	173	183	8.5 · 10^{-6}	
11 *	 $C_6H_5CH_2\underset{\displaystyle CH_3}{\underset{\vert}{CH}}$	H	111 (2)	1.0220	1.5462	60.51	60.42	195	192	—	
12	C_6H_5	H	118 (4)	1.6030	1.1019	48.07	48.17	153	147	4 · 10^{-10}	115
13	o-$CH_3C_6H_4$	H	132 (5)	1.5895	1.0751	52.71	52.47	167.2	166	2.5 · 10^{-10}	192
14 *	m-$CH_3C_3H_4$	H	133—134 (5)	1.5874	1.0680	52.67	52.71	167.2	164.5	4.9 · 10^{-10}	106
15	p-$CH_3C_6H_4$	H	130 (5)	1.5862	1.0664	52.71	52.65	167.2	168.4	1.2 · 10^{-9}	165
16	o-$CH_3OC_6H_4$	H	146 (5)	1.5918	1.1350	54.47	54.63	183.2	189	3 · 10^{-10}	153
17 *	m-$CH_3OC_6H_4$	H	163 (5)	1.5930	1.1464	54.47	54.20	183.2	182.2	1.5 · 10^{-9}	96
18	p-$CH_3OC_3H_4$	H	151 (4)	1.5910	1.1450	54.47	54.07	183.2	183.6	2 · 10^{-9}	146
19	o-$NH_2C_3H_4$	H	152 (1.5)	1.6320	1.1644	51.50	51.55	168.2	—	—	—
20	m-$NH_2C_6H_4$	H	165 (1.5)	1.6483	1.1765	51.50	52.02	168.2	167	—	206

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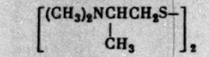
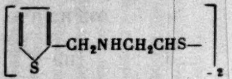
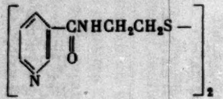
* Compound was prepared for the first time.

** For arylsubstituted compounds MR_D was calculated from Vogel's data.

*** Molecular weight was calculated from the potentiometric titration data on free bases.

TABLE 3

Properties of Some Aminodisulfides*

Compound No.	Formula	Boiling point (pressure in mm)	d_4^{20}	n_D^{20}	MR_D		Molecular weight (potentiometrically)		Melting point	Hydrochloride	
										Cl contents (in %)	
					calculated	found	calculated	found		calculated	found
1	$(H_2NCH_2CH_2S-)_2$	106—108 (5)	1.1559	1.5720	43.35	43.27	152	155	212°	32.0	31.8
2	$[(CH_3)_2NCH_2CH_2S-]_2$	132—135 (4)	0.9852	1.5109	62.4	63.2	208	216	222	25.26	25.76
3	$[(C_2H_5)_2NCH_2CH_2S-]_2$	115 (2)	0.9572	1.5000	80.89	81.11	264	260	206	21.06	20.45
4	 $\left[(CH_3)_2N\underset{\displaystyle CH_3}{\underset{\vert}{C}}HCH_2S-\right]_2$	128—131 (4)	0.9762	1.5030	71.3	71.8	236	239	—	—	—
5	$[(CH_3)_2NCH_2CH_2CH_2S-]_2$	Decomposes on distillation							188	23.0	22.97
6	$[H_2N(CH_2)_3S-]_2$	—	—	—	—	—	—	—	207	23.0	23.2
7		—	—	—	—	—	—	—	229	18.44	18.28
8		—	—	—	—	—	—	—	160	16.35	16.5

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*Compounds Nos. 4-8 were synthesized for the first time.

Bis-(N-dimethyl-β-aminoethyl)-disulfide. We placed 32 g of powdered sulfur and a saturated solution of sodium sulfide nonahydrate (240.2 g) in a three-necked flask supplied with a stirrer, a reflux condenser, and a dropping funnel. The mixture was heated till the sulfur completely dissolved. To the hot disulfide solution we added at 70° a saturated aqueous solution of N-dimethyl-β-chloroethylamine (144 g), and the mixture was kept for 3 hours at 70-80°. After that, the mixture was cooled to 40-50°, neutralized with 85 ml of concentrated hydrochloric acid, treated with 15 g of activated charcoal, and filtered. The colorless filtrate was evaporated to the first appearance of salt crystals, and made alkaline with 100 ml of 40% NaOH. The oil which floated up was separated, dried over anhydrous sodium sulfate and fractionally distilled in vacuum. The yield of disulfide was 82 g (78.8%).

Taurine (aminoethylsulfonic acid). To 11.3 g of β-mercaptoethylamine hydrochloride in 25 ml of acetic acid we slowly added a perhydrol—acetic acid mixture (50 ml of each). The temperature was maintained in the 45-50° range. After that, the solution was heated on a boiling water bath till the peroxide decomposed, and the volatile substances were distilled off in vacuum. The light-yellow residue was treated with an alcohol—acetone (1:4) mixture. The compound was filtered out. The m. p. was 315-320°. The yield 3.5 g (28%).

Found %: N 11.31; S 29.4. $C_2H_7O_3NS$. Calculated %: N 11.17; S 29.5.

We obtained a similar yield of N, N-diethyltaurine, m. p. 150° (from water).

2-Ethylthiazolidine. Propionaldehyde (17.4 g) and ethylenimine (12.9 g) were dissolved in 40 ml of methyl alcohol and saturated with hydrogen sulfide for 3-4 hours at −10°. After that, the solution was kept for 2 hours at room temperature. After repeated fractional distillation a compound with the following constants was ob-

B. p. 170-175°; d^{20}_4 1.0216, n_D 1.5135, MR_D 34.45; calc. 34.38.

Found %: S 27.34; N 11.96. $C_5H_{11}NS$. Calculated %: S 27.35; N 11.99.

Under similar conditions we prepared 2-propylthiazolidine from butyraldehyde. The b. p. was 74-75° (at 10 mm), d^{20}_4 0.9844, $n^{20}D$ 1.5030.

Ethylene sulfide. To an aqueous ethylene oxide solution (88 g in 100 ml of water) we added at 10° 76 g of thiourea over a period of 30 minutes; after that, we added to the mixture 100 ml of xylene, stirred the mass for 2 hours at 4-6°, separated the xylene layer, and treated the aqueous layer with another 100 ml of xylene. The combined xylene extracts were dried over calcium chloride. Distillation in an efficient fractionating column yielded a 45-62° fraction. Repeated fractionation yielded a 54-60° fraction. The yield was 40-44 g (65-70%), $n^{20}D$ 1.4900. Pure ethylene sulfide could be stored at 1-5° for over a month.

N-Substituted β-mercaptoethylamines. The synthesis was carried out by one of the below described methods. a) N,N-Dimethyl-β-mercaptoethylamine. A mixture consisting of dimethylamine (22.5 g, 0.5 mole), benzene (100 ml), and ethylene sulfide (30 g, 0.5 mole) was cooled to −15°, sealed in an ampule, and left for 24 hours at room temperature. After removing the polymer by fractional distillation we isolated 30 g (57%) of the compound, b. p. 123-126°.

b) N-Phenyl-β-mercaptoethylamine. A mixture consisting of aniline (14 g), ethylene sulfide (6 g), and ethyl alcohol (10 g) was sealed in an ampule and heated for 4 hours at 100°. After removing the solvent, we obtained by fractional distillation 11 g (72%) of the compound, b. p. 110-125° (at 47 mm).

SUMMARY

1. A detailed study of synthetic methods and properties of β-mercaptoethylamine makes this compound available for the preparation of a series of its derivatives and for pharmacological investigations.

2. A series of new N-substituted β-mercaptoethylamines were prepared by the reaction between ethylene sulfide and amines.

3. A method of preparing aminodisulfides from β-haloalkylamines and sodium disulfide was developed.

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CHLORINATION OF OLEFIN CHLOROHYDRINS

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The reaction of chlorine with olefin chlorohydrins has been studied but little. There is but one patent [1] which reports the possibility of preparation of chloral by chlorination of ethylene chlorohydrin. There are no data on the chlorination of propylene chlorohydrin. The aim of the present work was the study of chlorination reactions of ethylene and propylene chlorohydrins under various conditions. The present work is a continuation of a study of the chlorination of ethylene glycol [2]. We studied the chlorination of ethylene chlorohydrin as initiated by ultraviolet light at the temperatures of 30-40°, 60-70° and 90-100°; at 30-40° in the presence of 1% H_2O; at 50-60° in the presence of marble; and as initiated by 0.5% acetylcyclohexanesulfonyl peroxide [3] in the 70-80° range.

TABLE 1

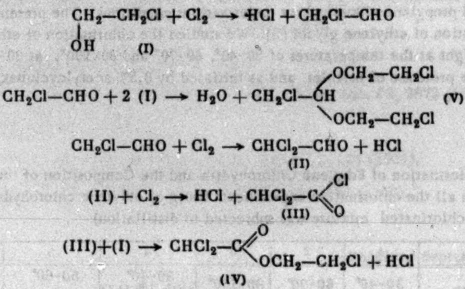
Results of Chlorination of Ethylene Chlorohydrin and the Composition of the Resulting Products. (In all the chlorination experiments 100 g of ethylene chlorohydrin was taken; 100 g of the chlorinated mixture was subjected to distillation)

Expt. No.	1	2	3	4	5	6
chlorination conditions	30-40° in u. v. light	60-70° in u. v. light	90-100° in u. v. light	30-40° with 1% H_2O in u. v. light	50-60° in u. v. light with marble	70-80° with 0.5% perox.
Duration of chlorination (hours)	6.5	25.0	9.0	3.5	4.0	4.5
Amount of chlorinated product obtained (in g)	119.0	116.0	119.5	131.5	105.5	112.0
Product of distillation of 100 g of mixture (in g)						
Of ethylene chlorohydrin	48.2	None	None	57.0	43.5	Traces
Of dichloroacetaldehyde	Traces	None	42.7	Traces	Traces	34.0
Of dichloroacetyl chloride	None	17.7	None	None	None	None
Of β-chloroethyl dichloroacetate	14.4	37.4	40.0	11.0	Traces	20.5
Di-(β-chloroethyl) acetal of chloroacetaldehyde	23.8	None	11.1	19.6	20.5	30.0
Distillation residue	11.1	10.4	0.75	3.21	8.8	9.2

The following compounds were isolated from the chlorination products and identified: ethylene chlorohydrin (I), dichloroacetaldehyde (II), dichloroacetyl chloride (III), β-chloroethyl dichloroacetate (IV), and di-(β-chloroethyl) acetal of chloroacetaldehyde (V). The data on the composition of mixtures formed under the conditions listed above are given in Table 1.

Insofar as β-chloroethyl dichloroacetate was found in all the experiments among the chlorination products along with either dichloroacetaldehyde or dichloroacetyl chloride, one may suppose that during the action of chlorine on (I) there occurs a process of oxidation and chlorination which is accompanied by secondary reactions of acetal or ester formation. Evidently, the first stage of the reaction of chlorine with (I) is the oxidation of the latter to chloroacetaldehyde. We failed to isolate free chloroacetaldehyde, but its formation cannot be doubted owing to the isolation of acetal (V) in the majority of the experiments. Chloroacetaldehyde is chlorinated further to dichloroacetaldehyde, which, with chlorine, forms the dichloroacetyl chloride. For the proof of this supposition we subjected dichloroacetaldehyde, prepared by chlorination of ethyl alcohol, to chlorination in ultraviolet light. Dichloroacetyl chloride was obtained as the result of this experiment. Dichloroacetyl chloride forms the corresponding ester with ethylene chlorohydrin.

Thus, the reaction of chlorine with ethylene chlorohydrin may be represented by the following reactions:



$$\underset{\text{OH}\quad(I)}{CH_2-CH_2Cl} + Cl_2 \longrightarrow HCl + CH_2Cl-CHO$$

$$CH_2Cl-CHO + 2\ (I) \longrightarrow H_2O + CH_2Cl-CH(OCH_2-CH_2Cl)_2 \quad (V)$$

$$CH_2Cl-CHO + Cl_2 \longrightarrow \underset{(II)}{CHCl_2-CHO} + HCl$$

$$(II) + Cl_2 \longrightarrow HCl + \underset{(III)}{CHCl_2-C(=O)Cl}$$

$$(III)+(I) \longrightarrow \underset{(IV)}{CHCl_2-C(=O)OCH_2-CH_2Cl} + HCl$$

The presence of 1% of water and the method of initiation do not affect the direction of the reaction materially. Chlorination of (I) in the presence of marble led predominantly to the formation of (V) owing to the catalytic action of the resulting calcium chloride [4].

Chlorination of 1-chloro-2-propanol, initiated by ultraviolet light, leads to the formation of a mixture of chloroketones. From this mixture we were able to isolate 1,1,3-trichloropropanone, which constituted 21% of the products chlorinated at 30-40°, and 37% of those chlorinated at 95-100°. No other individual chloroketones could be isolated.

EXPERIMENTAL

Ethylene chlorohydrin (b.p. 126-128° and $n^{20}D$ 1.4419) or propylene chlorohydrin (b.p. 128-130° and $n^{20}D$ 1.4334) obtained according to Michael [5] were loaded into a quartz reactor provided with a reflux condenser and a thermometer. Dry chlorine was introduced through a disperser made of a porous glass plate. The reactor was illuminated by a PRK-2 mercury quartz lamp set at the distance of 9 cm from the reactor. The chlorination was run until no further weight increase could be effected. Hydrogen chloride was removed by prolonged blowing with dry nitrogen. The products which were carried along by the nitrogen stream were caught in a trap kept at −60° to −70°. Then the products were kept over marble for several days.

The data on the chlorination of ethylene chlorohydrin and the composition of the chlorination products are given in Table 1. Ethylene chlorohydrin (I) isolated in experiments 1, 4 and 5 had b.p. 126-127° and $n^{20}D$ 1.4420. Ethylene oxide was obtained by dehydrochlorination with a sodium hydroxide solution. Dichloroacetaldehyde (II) isolated in experiments 3 and 6 and purified by triple distillation had b.p. 89.5-90.5° (b.p. 89.5-90.5 [6]).

Found %: Cl 62.53. $C_2H_2OCl_2$. Calculated %: Cl 62.83.

Six g of dichloroacetic acid was obtained in the oxidation of 6.5 g of (II) with concentrated nitric acid at 70-80°. The aniline salt of this acid had m.p. 123-124° (from benzene and alcohol). The mixed melting point with the aniline salt of dichloroacetic acid synthesized from chloral [7] showed no depression.

Dichloroacetyl chloride (III) was isolated in experiment 2; b.p. 107-108°, $n^{20}D$ 1.4600 (b.p. 107-108° [8]).

Found %: Cl 70.80; Cl (hydrolyzable) 22.80. C_2HOCl_3. Calculated %: Cl 72.20; Cl (hydrolyzable) 24.06.

From 3 g of (III) we obtained 1.2 g of dichloroacetamide (VI) with m.p. 98° (from benzene) (m.p. 98° [9]).

Found %: Cl 55.88; N 10.34. $C_2H_3ONCl_2$. Calculated %: Cl 55.46; N 10.93.

β-Chloroethyl dichloroacetate (IV) was isolated in experiments 1-4 and 6; b.p. 75-78° (5 mm), $n^{20}D$ 1.4722 (b.p. 209-212° at 767 mm [8]). By hydrolysis of 10 g of (IV) with a sodium hydroxide solution, followed by steam distillation, we detected ethylene oxide qualitatively (test with sodium chloride and phenolphthalein) and isolated 1.7 g of dichloroacetic acid, whose aniline salt had m.p. 123-124° (from benzene and alcohol). The mixed melting point with the aniline salt of dichloroacetic acid was not depressed.

Di-(β-chloroethyl)-acetal of chloroacetaldehyde (V) isolated in experiments 1 and 3-6 had the following constants:

b.p. 124-127° for 8 mm, $n^{20}D$ 1.4784, d^{20}_4 1.3250, M 219.31, MR_D 47.35; Calc. M 221.5, MR_D 47.79 (b.p. 134-135° for 10 mm, $n^{25}D$ 1.4757, d^{25}_4 1.320 [10]).

From 8.5 g of (V) we obtained, by cleavage with concentrated sulfuric acid and oxidation with 2% solution of potassium permanganate, 5.0 g of an acid whose aniline salt had m.p. 89-90° (from benzene). The mixed melting point with the aniline salt of chloroacetic acid was not depressed.

Chlorination of dichloroacetaldehyde (II). Dichloroacetaldehyde was prepared by chlorination of ethyl alcohol [11]. The chlorinated mixture was diluted with water and the hydrate of (II) was isolated from it by distillation through a fractionating column with a 20-theoretical-plate efficiency; from the hydrate we obtained (II) (b.p. 87.5 at 742 mm and $n^{20}D$ 1.4510) by two distillations with concentrated sulfuric acid and a distillation through a fractionating column with a 16-theoretical-plate efficiency. (II)(28.2 g) was placed in a quartz test-tube provided with a reflux condenser, a thermometer and a bubbler. The test tube was illuminated with the PRK-2 quartz mercury lamp set at the distance of 9 cm. The temperature was maintained spontaneously at 53° by the reaction mixture. The chlorination lasted for 13 hours. Hydrogen chloride was removed by keeping the product for several days over marble. As a result, we obtained 13.2 g of a product from which we were able to isolate by distillation 7.5 g of (III) which had b.p. 105-107° (b.p. 107-108° [8]).

Found %: Cl 71.05; Cl (hydrolyzable) 23.45. C_2HOCl_3. Calculated %: Cl 72.20; Cl (hydrolyzable) 24.06.

From 3.1 g of (III) we obtained 1.7 g of (VI) with m.p. 98° (from benzene [9]) (m.p. 98°).

Found %: Cl 54.85; N 10.74. $C_2H_3ONCl_2$. Calculated %: Cl 55.46; N 10.93.

Data on the chlorination of propylene chlorohydrin and the fractional composition of the resulting products are given in Table 2.

Fraction a from experiments 1 and 2 consisted of a mixture of mono- and dichloroacetones, which could not be separated since the difference in their boiling points was but 1°. The chlorine content in this fraction from experiment 1 was 46.52%, which corresponded to a mixture consisting of 53.5% of monochloroacetone and 46.50% of dichloroacetone. The chlorine content in this fraction from experiment 2 was 47.88%, which corresponded to a mixture of 45.75% of monochloroacetone and 54.25% of dichloroacetone.

From fraction b from both experiments we isolated 1,1,3-trichloropropanone (VII) with b.p. 60-63° at 3 mm, $n^{20}D$ 1.4900 (b.p. 172° [12]).

Found %: C 21.82; H 1.82; Cl 66.08. M 165.40 (cryoscopic). $C_3H_3OCl_3$. Calculated %: C 22.29; H 1.85; Cl 65.94. M 161.5.

We obtained 2.2 g of an acid whose aniline salt was identical with the aniline salt of dichloroacetic acid, by oxidation of 4.8 g of (VII) with 2% potassium permanganate solution. After the oxidation we found in the solution 1.077 g of chlorine by the mercurometric method, while calculation indicated that there should have been 1.055 g.

TABLE 2

Results of Chlorination of Propylene Chlorohydrin in Ultraviolet Light and the Fractional Composition of the Resulting Products (100 g of propylene chlorohydrin was taken for chlorination; 100 g of the chlorinated product was taken for the distillation)

Experiment No.	1	2
Reaction temperature	30-40°	95-100°
Duration of chlorination (hours)	14.5	15.5
Product obtained (g)	147.2	161.5
Fractional composition (g)		
a) 102-126° at 754 mm	41.3	18.55
b) 56-63° (3 mm)	21.7	37.30
c) 63-100° (3 mm)	11.1	13.65
Distillation residue (g)	9.7	12.8

We failed to isolate any individual substances from fraction c of either experiment. The chlorine content and the positive test for a carbonyl group gave grounds for supposing that this fraction was a mixture of more fully chlorinated ketones.

SUMMARY

1. In chlorination of ethylene chlorohydrin initiated by ultraviolet light or by acetylcyclohexanesulfonyl peroxide the following substances are formed: dichloroacetaldehyde, dichloroacetyl chloride, β-chloroethyl dichloroacetate and di-(β-chloroethyl)-acetal of chloroacetaldehyde. An explanation of formation of these products is given.

2. Chlorination of dichloroacetaldehyde initiated by ultraviolet light leads to the formation of dichloroacetyl chloride.

3. In chlorination of propylene chlorohydrin initiated by ultraviolet light at 30-100° a mixture of chloroketones was formed, from which we isolated and identified some 1,1,3-trichloropropanone.

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REACTION OF MERCURIC PIVALATE WITH PEROXIDES AND WITH LIGHT

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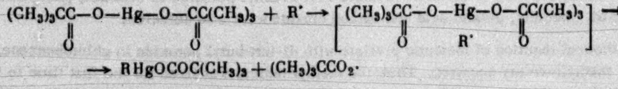
It was shown in the previously published papers [1-3] that mercuric salts of carboxylic acids undergo a decarboxylation reaction with formation of the corresponding organometallic compounds under the influence of peroxides or ultraviolet light. In the reaction of acetyl peroxide and some other peroxidic compounds with mercuric acetate and propionate the process has the radical chain character. In the present work we studied the reactions of mercuric pivalate (trimethylacetate) with benzoyl peroxide and with a dialkyl peroxide – di-tert-butyl peroxide – as well as with ultraviolet light.

The reaction of mercuric pivalate with benzoyl peroxide was run in a benzene solution at 80°. From this reaction we obtained phenylmercury compounds. The yield was 94.8% based on benzoyl peroxide. Metallic mercury (39.7%), pivalic acid (30%) and a small amount of tarry products were found among the reaction products. The reaction of di-tert-butyl peroxide with mercuric pivalate was run in chlorobenzene solution at the boiling point of the solvent. As shown recently [4], chlorobenzene is not a completely inert solvent for di-tert-butyl peroxide; nevertheless it is more convenient than other solvents. From the reaction we obtained methylmercury compounds (in 35.7% yield based on the original salt), metallic mercury (50.6%), pivalic acid (68.7%) and gas containing carbon dioxide. The methylmercury compounds were determined in a manner similar to that described previously [2]. Fixation of methyl radicals in the decomposition of di-tert-butyl peroxide was observed for the first time, insofar as we were able to determine.

Illumination of mercuric pivalate in benzene with ultraviolet light at 80° produced 86.5% of mercury, 53.6% of pivalic acid, a mercury-containing tar and a gas containing some carbon dioxide.

Since the products and their yields from the photoreaction of mercuric acetate in benzene and in acetic acid were distinctly different [3], we examined the effect of the addition of pivalic acid on the photoreaction of mercuric pivalate in benzene. The results of the experiment showed that pivalic acid does not noticeably effect the photoreaction of mercuric pivalate.

It is possible to suppose, on the basis of the data thus obtained, that the radical R· formed in the decomposition of the peroxide ruptures the O-Hg bond with formation of the corresponding $RHgOCOC(CH_3)_3$. In accord with the previous work [1], we may propose the following scheme:



$$(CH_3)_3C\underset{\underset{O}{\|}}{C}-O-Hg-O-\underset{\underset{O}{\|}}{C}C(CH_3)_3 + R^{\cdot} \rightarrow \left[(CH_3)_3C\underset{\underset{O}{\|}}{C}-O-\underset{R^{\cdot}}{Hg}-O-\underset{\underset{O}{\|}}{C}C(CH_3)_3\right] \rightarrow$$

$$\rightarrow RHgOCOC(CH_3)_3 + (CH_3)_3CCO_2\cdot$$

(where R = C_6H_5· and CH_3·*)

$(CH_3)_3CCO_2$· may decompose further with evolution of carbon dioxide and it may detach a hydrogen (the donor may be the initial salt). The presence of relatively large amounts of pivalic acid in the reaction products shows that a reaction of hydrogen redistribution in the pivalyloxy radical occurs to a considerable degree in this instance, this reaction predominating over the decomposition of the radical.

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*In accord with data of Vaughan and co-workers [5]: $(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO^{\cdot}$; $(CH_3)_3CO^{\cdot} \rightarrow CH_3 + CH_3COCH_3$.

The absence of compounds of tert-butylmercury in all cases among the reaction products must be explained evidently, by the fact that the secondary radicals formed in the decomposition of the salt [$(CH_3)_3CCO_2\cdot$ and $(CH_3)_3C\cdot$] are incapable of producing a subsequent decomposition of the mercuric pivalate. Such behavior of the tert-butyl radical is not unexpected; there are indications in the literature that this radical is not very reactive. Thus, for example, in the decomposition of dipivalyl peroxide in carbon tetrachloride, no formation of tert-butyl chloride was observed [6]. At the same time RCl was readily obtained in the reaction of carbon tetrachloride with other acyl peroxides [7, 8] (where R = CH_3, n-C_3H_7, iso-C_3H_7, etc.).

One should mention the presence in all the experiments of a large amount of metallic mercury and the absence of mercurous salts.

EXPERIMENTAL

Reaction of mercuric pivalate with di-tert. butyl peroxide in a chlorobenzene medium. Into a round-bottomed flask provided with a stirrer with a mercury seal and a reflux condenser connected to a burette for gas collection we placed 10.0 g of mercuric pivalate,* 5.1 g of di-tert-butyl peroxide with b.p. 109° and $n^{21}D$ 1.3893 (prepared according to Milas [10]) and 100 ml of freshly distilled chlorobenzene. The reaction mixture was refluxed for 24 hours. 470 ml of a gas was collected. It was found to contain carbon dioxide (clouding of barium hydroxide solution). The gas was not studied further. After completion of the reaction, 2.52 g (50.6 %) of metallic mercury was collected. The solvent was distilled off under vacuum. Among the distilled products we detected 1.58 g of pivalic acid. Steam was passed into the remaining portion. 1.90 g of pivalic acid was found in the distillate. Thus, the total weight of pivalic acid was 3.48 g (68.7%). From the distillate and from the residue after the steam distillation, we obtained methylmercury iodide, by addition of potassium iodide (3.04 g or 35.7% of the substance was obtained); it had m.p. 141°. The mixed melting point with pure methylmercury iodide was 142.5°. Some 2.25 g of tar was left in the distilling flask and this was not examined further.

Reaction of mercuric pivalate with benzoyl peroxide in a benzene medium. The experiment was run along the same lines as the previous one. We used for the reaction 10.0 g of mercuric pivalate, 1.57 g of benzoyl peroxide (activity 95%) and 125 ml of benzene. This was heated for ten hours at 80°. 282 ml of a gas was collected. The presence of carbon dioxide in it was shown. 1.98 g (39.7%) of mercury was collected.

By treatment of the reaction mixture with a potassium bromide solution we obtained 4.21 g of phenylmercury bromide, amounting to 94.8% yield as calculated on benzoyl peroxide (m.p. 275.5°, from acetone); the mixed melting point with authentic phenylmercury bromide was 276°. 1.54 g of pivalic acid was collected.

A photoreaction of mercuric pivalate in a benzene medium was carried out under conditions similar to those described previously [3]. 10.0 g of mercuric pivalate and 175 ml of benzene were used. Illumination time: 1.5 hours. 420 ml of gas was collected; the presence of carbon dioxide in it was shown. The weight of collected mercury was 4.31 g (86.5%). From the benzene solution we isolated 2.69 g (53.6%) of pivalic acid. We obtained 1.92 g of tar which contained 0.48 g of mercury. In running the photoreaction of mercuric pivalate in benzene with the addition of 5.0 g of pivalic acid we obtained the same substances in the same amounts as in the previous experiment (after subtraction of the added pivalic acid).

SUMMARY

1. In the thermal reaction of mercuric pivalate with benzoyl peroxide in benzene, phenylmercury compounds were formed. Mercury, pivalic acid and carbon dioxide were also detected.

2. In the thermal reaction of mercuric pivalate with di-tert-butyl peroxide in chlorobenzene, formation of compounds of methylmercury occurred. Thus, the methyl radical was fixed for the first time in the decomposition of di-tert-butyl peroxide in a liquid phase. Among the reaction products mercury, pivalic acid and carbon dioxide were also detected.

3. The photoreaction of mercuric pivalate in benzene was studied at 80°. It was shown that in photoreactions the decomposition of mercuric pivalate occurs with formation of mercury, pivalic acid, carbon dioxide and a tar which contains mercury.

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* Mercuric pivalate was prepared from sodium pivalate and mercuric nitrate [9]; m.p. 233° (after recrystallization from chloroform).

4. In thermal and photoreactions of mercuric pivalate, the formation of compounds of the type $(CH_3)_2CHgX$ was not observed.

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SYNTHESIS OF ACETYLCHOLINE LABELLED WITH RADIOACTIVE CARBON C^{14} IN THE ESTER GROUP

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Acetylcholine ($[(CH_3)_3\overset{+}{N}CH_2CH_2OCOCH_3]\overset{-}{O}H$ the acetic ester of trimethyl-β-hydroxyethylammonium hydroxide) is an effective parasympathomimetic substance and finds a wide area of application as a pilocarpine substitute. Recently a series of C^{14}-labelled esters of carboxylic acids and amino alcohols, with therapeutic significance, have been synthesized. In 1955 novocain, cocaine and anesthesin labelled with C^{14} in the ester group were prepared [1], while in 1957 spasmolytin was prepared, labelled with C^{14} both in the ester group [2] and in the amino alcohol residue [3]. Radioactive acetylcholine, labelled in the choline group, was prepared in 1951 [4]. For the purpose of biological studies we accomplished the synthesis of acetylcholine labelled with C^{14} in the ester group by the following scheme:

$$CH_2ClCH_2OH + (CH_3)_3N \longrightarrow [(CH_3)_3\overset{+}{N}CH_2CH_2OH]\overset{-}{Cl}$$

$$CH_3C^{14}OONa + ClCOCH_3 \longrightarrow CH_3C^{14}OOOCCH_3$$

$$[(CH_3)_3\overset{+}{N}CH_2CH_2OH]\overset{-}{Cl} + CH_3C^{14}OOOCCH_3 \longrightarrow$$

$$\longrightarrow [(CH_3)_3\overset{+}{N}CH_2CH_2OC^{14}OCH_3]\overset{-}{Cl}$$

The starting material for the radioactive synthesis was acetic acid labelled with C^{14} in the carboxyl group. The total radioactivity of the acetic acid in each experiment was 3-4 mC. Acetylation with acetic anhydride is usually run in the presence of acetic acid. It is therefore possible to suppose that molecules of this acid also take part in the acetylation reaction. Moreover, the possibilities of isotope exchange between molecules or of exchange of acetyl groups between the acid and the anhydride in the process of the reaction are not excluded. In view of these considerations, in our first experiments the acetylating mixture consisted of a nonradioactive anhydride and radioactive acid which had been first boiled for one hour. However, after acetylation of choline with such a mixture the resulting product was devoid of radioactive properties within the accuracy of the experiment. This fact proved that isotope exchange and exchange of acetyl groups did not occur under the conditions of the experiment and that acetic acid does not take part in the reaction of acetylation of choline, but acts only as a source of hydrogen ions which catalyze the esterification reaction.

EXPERIMENTAL

Synthesis of choline. Several methods of preparation of choline are known. We chose the method using trimethylamine and ethylene chlorohydrin [5], avoiding the use of sealed tubes and evaporation of aqueous solutions. Ethylene glycol (51 ml) was placed in a round-bottomed flask and heated in an oil bath to 145°. At this temperature a stream of dry hydrogen chloride was introduced into the reaction mixture. The temperature slowly rose to 163° and after some nine hours the ethylene chlorohydrin was distilled through a distilling condenser. After fractional distillation a fraction with b.p. 128-130° was obtained; yield: 45%.

A mixture of 15 g of ethylene chlorohydrin, 36 g of trimethylamine (3-fold excess) and anhydrous 100% ethyl alcohol* was set aside for several days. The reaction proceeded very slowly and only on the third day did the precipitation of choline hydrochloride begin. The precipitated choline hydrochloride was filtered with a Buchner funnel and was stored in a tightly closed vessel in a desiccator. For complete isolation of the product, the mother liquor was evaporated to 1/4 of original volume and absolute ether was added, with cooling, to precipitate the product in crystalline form. Yield: 65% theoretical.

Synthesis of radioactive acetylcholine. Six ml of $CH_3C^{14}OOH + CH_3CO_2H$ with specific activity of 4 mC/g was quantitatively neutralized with sodium hydroxide solution. After evaporation of the solution to dryness under a slight vacuum and heating of the resulting sodium acetate to 300°, the cooled salt was powdered and added to the calculated amount of acetyl chloride. The resulting radioactive acetic anhydride was distilled through a small column. Then, to 10 g of choline hydrochloride was added twice the theoretical amount of acetic anhydride labelled with C^{14} along with a small amount of glacial acetic acid. The mixture was refluxed for 20-25 minutes. When the mixture was cooled, crystals of acetylcholine hydrochloride began to form. After removal of acetic acid and unreacted anhydride, a ten-fold amount of absolute ether was added for complete separation of the product. Some cases were observed in which the acetylcholine failed to crystallize but precipitated as an oily mass. After seeding with a single crystal and rubbing of the flask walls with a glass rod, the substance began to crystallize. The crystallization sometimes was complete in 20-30 minutes, at other times it lasted for some hours. Acetylcholine was rapidly filtered off on a porous glass funnel, closed with a calcium chloride tube, was then washed with absolute ether and dried in a vacuum over sulfuric acid. The radioactivity yield, calculated on the starting acid was 25%.

Found %: Cl 18.9; N 7.25. $C_7H_{16}O_2NCl$. Calculated %: Cl 18.8; N 7.48.

SUMMARY

1. Choline was synthesized from ethylene chlorohydrin and trimethylamine by a method which produced a 65% yield.

2. Synthesis of acetylcholine hydrochloride was accomplished for the product labelled with radiocarbon C^{14} in the ester group, by the way of acetylation of choline hydrochloride with a radioactive specimen of acetic anhydride.

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*Even insignificant amounts of water prevent the crystallization of choline salts.

**Original Russian pagination. See C. B. Translation.

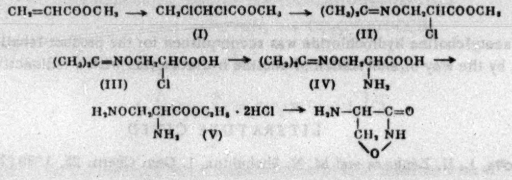
CYCLOSERINE AND RELATED COMPOUNDS

III. SYNTHESIS OF CYCLOSERINE*

N. K. Kochetkov, R. M. Khomutov, M. Ia. Karpeiskii and E. I. Budovskii

Recently we reported briefly [2] a new synthesis of the antibiotic cycloserine (D-4-aminoisoxalid-3-one) starting with the readily available ester of α,β-dichloropropionic acid and acetoxime. Owing to the confirmation of the high antitubercular activity of the substance by an experimental study of cycloserine [3] and by a series of clinical data [4], we studied this method of preparation of cycloserine in detail. All the syntheses of cycloserine published to this data by other authors [5-7] start with the difficultly accessible amino acid – serine.

We accomplished the synthesis of cycloserine in accordance with the above scheme, with the starting material being the methyl ester of acrylic acid.



$$CH_2{=}CHCOOCH_3 \longrightarrow \underset{(I)}{CH_2ClCHClCOOCH_3} \longrightarrow \underset{(II)}{(CH_3)_2C{=}NOCH_2\underset{Cl}{\underset{|}{C}H}COOCH_3}$$

$$\underset{(III)}{(CH_3)_2C{=}NOCH_2\underset{Cl}{\underset{|}{C}H}COOH} \longrightarrow \underset{(IV)}{(CH_3)_2C{=}NOCH_2\underset{NH_2}{\underset{|}{C}H}COOH} \longrightarrow$$

$$\underset{(V)}{H_2NOCH_2\underset{NH_2}{\underset{|}{C}H}COOC_2H_5 \cdot 2HCl} \longrightarrow$$

The most difficult part of the synthesis is the condensation of the methyl ester of α,β-dichloropropionic acid (I) with acetoxime. The difficulties of this reaction are connected with the fact that it must be accomplished with a selective substitution of the β-halogen atom. It must be noted that the reaction of esters of α,β-dihalo carboxylic acids with basic reagents proceeds, as a rule, in a rather complex fashion with formation of a mixture of substances and the proportions of the final products depend on an entire series of factors [8].

We studied the reaction of (I) with acetoxime in the presence of various condensing agents (sodium alcoholates, lithium and magnesium alcoholates, sodium hydroxide, potassium hydroxide, pyridine) in polar and nonpolar solvents (water, alcohols, dioxane, ether, etc.) at various temperatures and with various proportions of the reactants. The best results were obtained by the condensation of (I) with the oxime in the presence of sodium methoxide in methanol at 0-5°; in this case the yield of (II) reached 25-30%. Besides (II) we were able to isolate from the reaction mixture, in 20% yield, the reaction product of sodium methoxide with (I) – the methyl ester of α-chloro-β-methoxypropionic acid. Along with the latter substance, the methyl ester of α-chloroacrylic acid and the product of alkylation of acetoxime at the nitrogen atom are evidently formed.

The question as to the true mechanism of the reaction of substitution of the β-halogen atom in (I) remains open since the literature lacks any definite data on the mechanism of substitution of the halogen atom in β-halo acids, β-halo ketones and similar compounds. Among the two alternate possibilities – direct nucleophilic attack of the anion at the β-carbon atom and the preliminary cleavage of the hydrogen halide with the subsequent addition of the resulting α-haloacrylate at the double bond – we are inclined to choose the latter.

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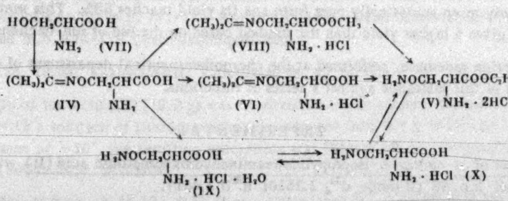
*For Parts I and II see [1, 2].

The fact that our attempt to run a condensation of acetoxime with an ester of α, β-dichloroisobutyric acid (which is incapable of eliminating its β-halogen as a hydrogen halide) under the same conditions did not produce a substitution reaction supports this view. In running this reaction under considerably more drastic conditions (refluxing in methanol for several hours) only the ester of the methoxychloroisobutyric acid was isolated; in this case one may suppose that the tertiary α-halogen atom underwent the substitution reaction.

The next step in the synthesis of cycloserine is the amination. Since an attempt at direct amination of the methyl ester of α-chloro-β-isopropylideneaminohydroxypropionic acid (II) in liquid ammonia did not give the desired result at room temperature [9], ester (II) was first saponified with alkali to the corresponding acid (III), which was then subjected to amination. Amination of acid (III) in aqueous or alcoholic solutions of ammonia at various temperatures either did not occur or was accompanied by decomposition, owing to which we failed to isolate the amino acid (IV) in any significant amounts. Analogous results were obtained in running the reaction with aqueous ammoniacal solutions of ammonium carbonate. Only by heating acid (III) with excess liquid ammonia (in the presence of ammonium nitrate) were we able to accomplish the ammonolysis of the α-halogen atom and to obtain β-isopropylideneaminohydroxyalanine (IV) in 40-50% yields. We established that the yield of the amino acid depends essentially on the material of which the autoclave is constructed – the best results were obtained in working with autoclaves made of stainless steel. In comparison with the original variant [2], the method of isolation of the amino acid (IV) from the reaction mixture was simplified considerably. Acid (IV) was isolated as the hydrochloride which then served as the fundamental substance for the preparation of the dihydrochloride (V) (see below). If needed, amino acid (IV) could be obtained by treatment of the hydrochloride with lithium methoxide.

One of the most complicated operations in the synthesis of cycloserine was the transition from amino acid (IV) to the dihydrochloride of the ester of β-aminohydroxyalanine (V) which step is connected with the possibility of the most diverse transformations of (IV) in the presence of acid reagents.

For selection of the most dependable and rational path for the transition from (IV) to (V) we studied the behavior of (IV) under various conditions of acid hydrolysis.



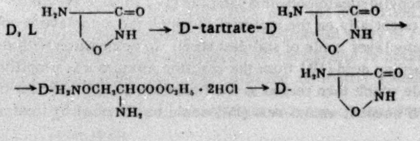
In drastic hydrolysis of the amino acid (IV) (refluxing four hours with concentrated hydrochloric acid) there occurs a total decomposition of the isopropylideneaminohydroxy group as the result of which serine (VII) is formed. In the cold, however, the formation of the hydrochloride of β-isopropylideneaminohydroxyalanine (VI) takes place. In treatment of (IV) with an alcoholic solution of hydrogen chloride at room temperature the esterification of (IV) takes place with formation of ester (VIII) as the main product. We found that the conditions (hydrolysis with a mixture of methanol and concentrated hydrochloric acid, (1 : 1) under which the cleavage of the isopropylidene group in the form of acetone occurs, do not cause the accompanying destruction of the aminohydroxy group.

The reaction produced β-aminohydroxyalanine hydrochloride in a yield of over 50%, the product being isolated in the form of its monohydrate (IX) with m.p. 141-142°; drying the latter under vacuum at 65° over phosphoric anhydride gave the anhydrous hydrochloride (X). It is interesting to note that (X) is the lowest homolog of canaline $H_2NOCH_2CH_2CH(NH_2)COOH$, which, according to the available data, has a definite physiological activity [10].* In esterification of (IX) and (X), (V) is formed in high yield; the acid hydrolysis of this leads again to (IX) and (X).

We established that the preparation of (V) is realized most satisfactorily by starting with (VI). The latter is hydrolyzed by 3-hour reflux with a mixture of methanol and concentrated hydrochloric acid (1 : 1) with a subsequent esterification, during which (IX) and (X) are not isolated in the pure state. This variant of the synthesis is more convenient than that presented by us previously [2]; in this case it is better to prepare not the methyl ester [1, 2], but the ethyl ester of β-aminohydroxyalanine, the yield of which reaches 50-60% based on (VI). Dihydrochloride (V) may be also prepared directly from (IV) or (VIII).

In the last step – cyclization of dihydrochloride (V) into cycloserine – we succeeded in raising the yield of the antibiotic from 65% to 82%, while D,L-cycloserine was isolated from the reaction mixture directly in an analytically pure state. The reaction was effected by the heating (10-12 minutes) of (V) with a two-fold excess of an alcoholic solution of potassium hydroxide.

D-4-Amino-3-isoxalidone was prepared from the cycloserine racemate by the following scheme:



The racemate was treated in aqueous solution under strictly defined conditions of concentration and temperature with D-tartaric acid. The quantitatively separated D-tartrate of D-4-amino-3-isoxazolidone was transformed into the dihydrochloride of the ethyl ester of D-(β-aminohydroxy)-alanine by heating with an alcoholic solution of hydrogen chloride. The resulting dihydrochloride was cyclized in the usual manner into 4-amino-3-isoxazolidone whose properties were completely identical with those of the natural antibiotic.

The method of separation of the product, as accomplished by us, is very simple experimentally: cycloserine is obtained immediately in an analytically pure form and its yield reaches 53%. This method is considerably more convenient and gives a higher yield than the method based on the use of ion-exchange resins [5, 10].

Tests of cycloserine racemate, performed at the chemotherapeutical department of our institute, showed the high effectiveness of this substance against a series of infections.

EXPERIMENTAL

The methyl ester of α-chloro-β-isopropylideneaminohydroxypropionic acid (II) was prepared according to [2] in 25-26% yield; b.p. 79° (2 mm); d^{20}_4 1.1510; $n^{20}D$ 1.4517.

Found %: N 7.14; Cl 18.31. $C_7H_{12}O_3NCl$. Calculated %: N 7.20; Cl 18.31.

By treatment of the ester with liquid ammonia in an autoclave at room temperature, the corresponding amide was obtained; m.p. 91-92° (from ether).

Found %: C 40.25; H 6.32; N 15.70; Cl 19.73. $C_6H_{11}O_2N_2Cl$. Calculated %: C 40.34; H 6.20; N 15.67; Cl 19.85.

As a byproduct, a fraction with b.p. 54-56° (7 mm) was isolated, which consisted of the methyl ester of α-chloro-β-methoxypropionic acid. Yield: 180-185 g (20%).

Found %: C 39.32; H 6.17; Cl 22.53. $C_5H_9O_3Cl$. Calculated %: C 39.23; H 5.94; Cl 22.33.

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* Recently, in connection with the establishment of the diverse biological action of the natural amino acid – canavanine, $H_2NC(=NH)NHOCH_2CH_2CH(NH_2)COOH$ – some attempts at synthesis of (X) were undertaken; these were not successful [11].

α-Chloro-β-isopropylideneaminohydroxypropionic acid (III). Into a one-liter round-bottomed flask provided with a stirrer, a dropping funnel and a thermometer, we placed 360 g of the ester (II) and 300 ml of water, after which we added, with stirring and cooling, 360 ml of 5 N aqueous solution of sodium hydroxide, while maintaining the temperature of the reaction mixture at not above 25°. Then the reaction mixture was cooled to 10° and 73 ml of concentrated sulfuric acid was added to it, with stirring, at such a rate that the temperature did not rise above 20-25°. After the addition of sulfuric acid was completed, the mixture was filtered, the filtrate extracted with ethylene chloride (3 · 200 ml) and the combined extracts were dried over calcium chloride, the solvent distilled off, and 306 g (92%) of crude (III) was obtained.

Pure (III) has m.p. 43-44° and b.p. 113° (1 mm).

Found %: Cl 20.03. $C_6H_{10}O_3NCl$. Calculated %: Cl 19.74.

The ammonium salt was prepared by saturation of an ethereal solution of the acid with dry ammonia; m.p. 98-99° (from a mixture of acetone and benzene).

Found %: Cl 17.72. $C_6H_{13}O_3N_2Cl$. Calculated %: Cl 18.02.

β-Isopropylideneaminohydroxyalanine (IV). Into a glass vessel, cooled with a mixture of solid carbon dioxide and methanol, we placed 200 ml of liquid ammonia and carefully added, with stirring, 216 g of the crude chloro acid. After the termination of the vigorous reaction, we added 300 additional ml of liquid ammonia and 2 g of ammonium nitrate; the mixture was stirred and the reaction vessel was placed into a previously chilled 2-liter steel autoclave provided with a valve and a sleeve for a thermocouple; the vessel was closed with a glass lid and the autoclave was sealed shut. After standing overnight, the autoclave was heated for 8-10 hours at 55-65° (pressure: 30-40 atmos.). After heating was completed, the autoclave was cooled to room temperature over 14-16 hours. Then the reaction mixture was transferred from the autoclave into a one-liter round-bottomed flask, provided with a reflux condenser. Ammonia was evaporated and to the residue was added 300 ml of alcohol, after which the whole was refluxed on a water bath for 30-45 minutes, cooled and separated from the crystalline precipitate, which was washed with 200 ml of cold alcohol. The resulting residual mixture of ammonium chloride and the amino acid was suspended in 125 ml of methanol, treated with the calculated amount of methanolic solution of hydrogen chloride, stirred thoroughly, and treated with 150 m- of butanol. After that, the reaction mixture was heated for a few minutes on a water bath, cooled, and filtered from ammonium chloride. Some 250-300 ml of alcohol was then distilled from the filtrate by heating on a water bath under 50-60 mm vacuum, the residue was cooled, and the precipitated hydrochloride was filtered off and washed with 75 ml of butanol. The yield of the hydrochloride with m.p. 172-174° was 104 g (44%). After recrystallization from anhydrous isopropyl alcohol, it had m.p. 175-176° (with decomposition).

Found %: Cl 18.28, 18.38. $C_6H_{13}O_3N_2Cl$. Calculated %: Cl 18.02.

The hydrochloride of the acid (IV) (19.6 g) was dissolved in the minimum volume of warm anhydrous methanol and treated with a solution of lithium methoxide prepared from 0.7 g of lithium and 30 ml of methanol. After standing for 48 hours at −10°, the resulting precipitate was filtered off and recrystallized from 92% ethanol. Yield of (IV): 12.9 g (80%); m.p. 251-252°.

Found %: C 45.22; H 7.45 N 17.33. $C_6H_{12}O_3N_2$. Calculated %: C 44.98; H 7.55; N 17.48.

β-Aminohydroxyalanine.

A. From acid (IV). (IV) (4.8 g) was refluxed with a mixture of 30 ml of concentrated hydrochloric acid and 30 ml of methanol for three hours with distillation of the resulting acetone. Then the mixture was clarified with carbon, evaporated to dryness and dried in vacuum over phosphorus pentoxide and alkali. The glassy hygroscopic residue was dissolved with warming in 10 ml of anhydrous alcohol, treated with 5 ml of anhydrous isopropyl alcohol, followed by hot water until it became clear. On standing, a crystalline precipitate formed, which was separated, washed with anhydrous alcohol and dried. Yield of (IX): 2.9 g (56%). After recrystallization from water: m.p. 141-142°.

Found %: Cl 20.45; N 15.83. $C_3H_{13}O_4N_2Cl$. Calculated %: Cl 20.07; N 15.86.

The product was a colorless crystalline substance, soluble in water and insoluble in organic solvents.

Drying of 0.5 g of (IX) in vacuum over phosphorus pentoxide at 65° for three hours gave (X).

Found %: Cl 21.12. $C_3H_{11}O_3N_2Cl$. Calculated %: Cl 21.30.

B. From dihydrochloride of the ester of aminohydroxyalanine (V). (V) (2.2 g) was dissolved in 50 ml of 10% hydrochloric acid and refluxed for one hour. Then the solution was evaporated under vacuum and the residue was recrystallized from aqueous alcohol. Yield of (IX): 1.1 g (70%); m.p. 141-143°.

Found %: N 16.10; Cl 20.44. $C_3H_{11}O_4N_2Cl$. Calculated %: N 15.86; Cl 20.07.

Methyl ester of acid (IV). (IV) (1.6 g) was suspended in 30 ml of anhydrous methanol and a rapid stream of dry hydrogen chloride was passed through the reaction mixture until the latter was saturated. After two days the homogeneous solution was evaporated to dryness under vacuum and the residue, after being dried over phosphorus pentoxide and alkali, was recrystallized from dry acetone. The yield of the pure methyl ester of acid (IV) was 1.1 g (65%); m.p. 143-145°.

Found %: C 40.28; H 6.77; Cl 17.01. $C_7H_{15}O_3N_2Cl$. Calculated %: C 39.91; H 7.18; Cl 16.83.

Preparation of Dihydrochloride of the Ethyl Ester of β-Hydroxyaminoalanine (V).

A. From hydrochloride of the amino acid (IV). A solution of 79.4 g of the hydrochloride of the amino acid (IV) in 600 ml of the hydrolysis mixture (concentrated hydrochloric acid and methanol in 1 : 1 ratio) was refluxed for three hours with a distilling column, with slow collection of the acetone which distilled during the process. Then, the reaction mixture was clarified with carbon, evaporated to dryness under vacuum, the residue was dissolved with heating in 400 ml of anhydrous alcohol and 100-120 ml of ethanol was distilled from the solution. Then a rapid stream of dry hydrogen chloride was passed for 1-1.5 hours through the boiling reaction mixture. The resulting crystalline precipitate was filtered off on the following day, washed with 100 ml of butanol and dried under vacuum over phosphorus pentoxide and alkali. The yield of (V) was 50.2 g (56%); m.p. 153-154° (from alcohol).

Found %: C 27.14; H 6.50; N 12.55; Cl 32.36. $C_5H_{14}O_3N_2Cl_2$. Calculated %: C 27.13; H 6.38; N 12.61; Cl 32.07.

B. From amino acid (IV). 6.6 g (60%) of (V), with m.p. 152-153°, was obtained analogously to the above experiment from 8.0 g of (IV).

C. From hydrochloride of the methyl ester of β-isopropylideneaminohydroxyalanine. There was obtained a 4.4 g yield (50%) of (V), with m.p. 151-153°, from 8.4 g of the hydrochloride of the ester of the amino acid, by a procedure described in section A above.

D. From the hydrochloride of β-aminohydroxyalanine (IX). One g of (IX) was suspended in 40 ml of anhydrous alcohol and refluxed for 1.5 hours, while a rapid stream of dry hydrogen chloride was passed into the mixture. After standing for 48 hours, the crystalline precipitate was filtered off, washed with anhydrous alcohol and dried under vacuum over phosphoric anhydride and alkali. The yield of (V) was 1 g (75%); m.p. 153-154°. Mixed melting point with authentic (V) was not depressed.

Found %: Cl 32.38, 32.38. $C_5H_{14}O_3N_2Cl_2$. Calculated %: Cl 32.07.

D,L-4-Amino-3-isoxazolidone (racemate of cycloserine). (V) (44 g) was dissolved in 50 ml of warm methanol and to this solution there was gradually added, with stirring, 400 ml of 2 N solution of potassium hydroxide in methanol. The reaction mixture was cooled, separated from potassium chloride, the filtrate refluxed for 10-15 minutes, clarified with carbon, and cooled. A solution of acetic acid in methanol was added until the pH 5.5-6 was reached. After standing for one hour, the precipitated racemate of cycloserine was filtered off and washed with 50 ml of cold methanol. The yield of pure D,L-cycloserine was 16.5 g (82%); m.p. 138-141° (with decomposition).

Found %: C 35.11; H 6.00; N 27.16. $C_3H_6O_2N_2$. Calculated %: C 35.29; H 5.92; N 27.45.

The product was a colorless crystalline substance with weakly acid taste; it was readily soluble in water and but insignificantly soluble in methyl alcohol; it was insoluble in the usual organic solvents. Cycloserine gave a silver salt which precipitated in the form of a colorless, rapidly darkening precipitate upon treatment of the substance with silver nitrate; the acid gave a cherry-red color with an aqueous solution of ferric chloride and a characteristic blue color with a solution of sodium nitroprusside.

Picrate. Picric acid (1.2 g) was dissolved with heating in 10 ml of anhydrous alcohol and to the hot solution there was added 0.25 g of cycloserine; the whole was refluxed for 5-10 minutes, filtered, kept for 24 hours at 0°, and the crystalline precipitate of the picrate collected. The yield: 0.5 g; m.p. 176-177°.

Found %: N 20.89. $C_9H_9O_9N_5$. Calculated %: N 21.14.

D-4-Amino-3-isoxazolidone (cycloserine). To a mixture of 4 g of D,L-cycloserine and 15 ml of water there was added in small portions, with stirring, 7 g of D-tartaric acid (the temperature being kept below 25°). The reaction mixture was then kept for 24 hours at 0-5°, the crystalline precipitate was separated, washed with two portions of 2 ml of cold water, then with 50% aqueous alcohol and with absolute alcohol, after which it was dried under vacuum over phosphoric anhydride. The yield of the D-tartrate of D-cycloserine was 5 g; m.p. 162°; $[\alpha]^{20}D$ + 40° (c 0.7 in water).

One g of D-tartrate of D-cycloserine was suspended in 30-50 ml of anhydrous alcohol and refluxed while being saturated with dry hydrogen chloride until the salt dissolved. After standing at room temperature for 48 hours, the mixture was heated to boiling and was filtered. The filtrate was evaporated to dryness and the residue was recrystallized from anhydrous alcohol. The yield of the dihydrochloride of the ethyl ester of D-β-aminohydroxyalanine was 0.5 g (60%); m.p. 159-161°; $[\alpha]^{20}D$ + 13°.

The dihydrochloride of the ethyl ester of D-β-aminohydroxyalanine (0.44 g) was dissolved in the minimum volume of absolute methanol, treated with 4 ml of 2N alcoholic solution of potassium hydroxide, filtered, and boiled for ten minutes. After being cooled, the mixture was neutralized with glacial acetic acid to pH 5.5-6 and was allowed to stand for two hours at 0°. The resulting crystalline precipitate was separated, washed with absolute methanol, and dried. The yield of D-4-amino-3-isoxazolidone was 0.17 g (85%) (53% based on the racemate); m.p. 153-155°; $[\alpha]^{20}D$ + 106° (c 1.17 in water).

SUMMARY

1. A synthesis of cycloserine from the ester of α, β-dichloropropionic acid was developed.

2. A D-4-amino-3-isoxazolidone, which was completely identical with the natural antibiotic, was prepared by an original method through the tartrate salt from the racemate of cycloserine.

3. The lowest homalog of canaline has been synthisized.

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A NEW REACTION OF α-PYRONES. SYNTHESIS OF VINYLOGS OF β-OXO ACID ESTERS

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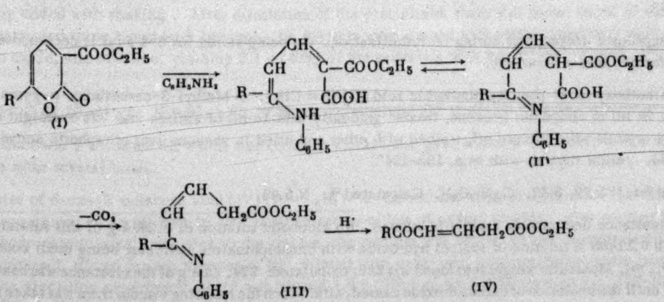
As it is already known, the cyclic system of α-pyrone is prone to be opened, under certain conditions of action of certain reagents [1, 2], to yield compounds of the aliphatic series. In this paper we described a new reaction connected with the opening of the α-pyrone ring, a reaction which permitted us to prepare the heretofore unknown vinylogs of esters of β-oxo acids.

We failed to prepare the amides or arylamides of 6-alkyl-2-pyrone-3-carboxylic acids by the direct action of ammonia or aromatic amines on the esters of these acids [3].

Thus, treatment of 6-methyl-3-carbethoxy-2-pyrone with aniline in benzene solution gave an unstable substance with m.p. 123-124°. The elemental analysis and the determination of the molecular weight of this substance indicated that it was the addition product of one mole of aniline with one mole of the carbethoxypyrone; for this reason, the anilide structure had to be rejected.

When this substance was heated, decarboxylation occurred and the residue readily lost aniline after being treated with an acid, the aniline being isolated in the form of its hydrochloride. This proved the presence of a free carboxyl group in this compound and spoke for the presence of an imino bond. Thus, it became clear that in the treatment of carbethoxypyrone (I) ($R=CH_3$) with aniline, the pyrone ring is opened.

By careful decarboxylation of the reaction product of carbethoxypyrone (I) ($R=CH_3$) with aniline it is possible to isolate, in the pure state, a substance with m.p. 104-105°, the analysis of which corresponds exactly to the data required for the ethyl ester of δ-N-phenylaminosorbic acid (III) ($R=CH_3$). The correctness of this conclusion about the structure of this substance was confirmed by the very mild conditions of hydrolysis, which when run in a mixture of dilute hydrochloric acid and ether gave about a 40% yield of the previously unknown vinylog of the acetoacetic ester – ethyl ester of 5-oxo-3-hexenoic acid (IV) ($R=CH_3$). Thus, the entire course of the transformation of 6-methyl-3-carbethoxy-2-pyrone into the vinylog of the acetoacetic ester may be presented by the following scheme:



In the reaction of (I) (R=CH_3) with an aqueous solution of ammonia there is formed a substance with m.p. 89°, which decomposes rapidly with evolution of ammonia; the analysis of this substance corresponded to the elemental composition of $C_8H_{13}O_2N$ and the substance is the ethyl ester of δ-aminosorbic acid. Its formation proceeds according to the scheme similar to that shown above, with the difference in that the opening of the pyrone ring is accompanied, in this case, by a spontaneous decarboxylation of the initial product of ring opening, i. e., product of type (II) (H in place of C_6H_5).

The new reaction, discovered by us, involves the opening of the α-pyrone ring and has a general character. Thus, 6-propyl-3-carbethoxy-2-pyrone (I) (R=C_3H_7) gave the corresponding (II) (R=C_3H_7) after being treated with aniline in alcoholic solution and the product, after having been decarboxylated and hydrolyzed with hydrochloric acid (in this case III need not be even isolated), gave the ethyl ester of 5-oxo-3-octenoic acid (IV) (R=C_3H_7). A completely analogous treatment of 6-amyl-3-carbethoxy-2-pyrone (I) (R=C_5H_{11}) gave the ethyl ester of 5-oxo-3-decenoic acid (IV) (R=C_5H_{11}).

The vinylogs of β-oxo acids, prepared in this manner, are colorless substances which are stable enough in storage in the liquid state, and which gradually turn dark only after the passage of some considerable time. They do not give an instantaneous color test with ferric chloride, but the color does appear after some time. The correctness of the location of the double bond in the formulas of these substances (IV), shown in the reaction schemes above, must be understood to have the same limitations as are imposed on the existing possibilities for tautomerism, in which it is possible to have a migration of the double bond from the α- and β-positions in respect to the carbethoxy group with formation of a diene system of the type shown by the enolic forms of the acetoacetic ester. This most interesting problem requires some further study as its solution is quite difficult.

Recently, R. A. Aleeva [4], as well as one of us and B. P. Gottikh [5], had accomplished a synthesis of the vinylogs of α-alkyl-β-oxo acids, but the simplest unsubstituted representatives of this class of compounds remained inaccessible up to the present. The method of synthesis of the latter compounds, as proposed in the present paper, makes these compounds quite readily available since the carbethoxypyrones, used as the starting materials, are readily prepared by the direct method from β-chlorovinyl ketones, a method developed by us previously [3]. One may hope that a study of the chemical behavior of the substance prepared by us may permit the future collection of new facts useful for the understanding of the problems of tautomerism and dual reactivity of organic compounds. It should be added also that the synthetic method proposed by us here is also suitable for the preparation of esters of δ-amino- and δ-arylaminodienic acids which are vinylogs of compounds of the type of aminocrotonic esters. This class of compounds, two of which are described for the first time in the present paper, are new types of ene-amino compounds and are interesting for the solution of some general problems.

EXPERIMENTAL

Ethyl ester of δ-aminosorbic acid. 6-Methyl-3-carbethoxy-α-pyrone (3.18 g) was dissolved in 75 ml of concentrated aqueous ammonia and after five hours the precipitated crystals were filtered off, washed with cold water and dried in vacuum over phosphoric anhydride. Yield: 1.33 g (51%); yellow crystals with m.p. 89°.

Found %: C 62.25, 62.43; H 8.49, 8.53; N 9.43, 9.35. $C_8H_{13}O_2N$. Calculated %: C 61.91; H 8.45; N 9.03.

The substance decomposes during recrystallization. On being stored for 3-4 days it decomposes completely, being transformed into a brown tar.

α-Carbethoxy-δ-N-phenylaminosorbic acid (II) (R=CH_3). 6-Methyl-3-carbethoxy-α-pyrone (26 g) was dissolved in 20 ml of anhydrous benzene, treated gradually with 14 ml of aniline and left overnight at 0°. The precipitated crystals were filtered off, washed with ether and dried in vacuum over phosphoric anhydride. Yield: 30.7 g (78%); yellow crystals with m.p. 123-124°.

Found %: N 5.22, 5.17. $C_{15}H_{17}O_4N$. Calculated %: N 5.09.

The substance decomposes rapidly in storage. An alcoholic solution of 0.2904 g of this substance was titrated with 0.11405 N solution of sodium hydroxide with phenolphthalein indicator being used; consumption of NaOH was 9.1 ml. Molecular weight thus found was 280; calculated: 274. One g of the substance was heated in an oil bath to 120° until the evolution of carbon dioxide ceased, after which the resulting viscous mass was taken up in ether and the solution was saturated with dry hydrogen chloride with cooling. Crystals of aniline hydrochloride precipitated immediately with considerable evolution of heat; m. p. 196°; mixed melting point with an authentic sample gave no depression.

2-Carbethoxy-5-N-phenylamino-2,4-octadienoic acid (II) (R= C_3H_7). 6-Propyl-3-carbethoxy-α-pyrone (23.8 g) was mixed with 11.4 g of aniline in 25 ml of alcohol. On the following day the solidified reaction mixture was diluted with ether, the crystals were filtered off and dried in vacuum over phosphoric anhydride. Yield: 25.0 g (82%); yellow crystals with m.p. 107-108° (with decomposition) (from alcohol).

Found %: C 67.18, 66.98; H 7.05, 6.99; N 4.65, 4.66. $C_{17}H_{21}O_4N$. Calculated %: C 67.30; H 6.98; N 4.62.

The compound dissolves in hot alcohol, difficultly in chloroform and is insoluble in water and ether.

2-Carbethoxy-5-N-phenylamino-2,4-decadienoic acid (II) (R= C_5H_{11}). To 61.8 g of 6-amyl-3-carbethoxy-α-pyrone in 120 ml of alcohol there was added 28 ml of aniline and the mixture was left overnight at 0°. After the usual treatment there was obtained 33.1 g (36%) of yellow crystals with m.p. 106-107° (from alcohol).

Found %: C 69.16, 69.28; H 7.80, 7.78; N 4.30, 4.48. $C_{19}H_{25}O_4N$. Calculated %: C 68.86; H 7.60; N 4.23.

The compound dissolves in hot alcohol and with difficulty in cold alcohol; it is insoluble in water and ether.

Ethyl ester of δ-N-phenylaminosorbic acid (III) (R = CH_3). α-Carbethoxy-δ-N-phenylaminosorbic acid (30.7 g) was heated in an oil bath to 130° until the evolution of carbon dioxide ceased; after cooling, some ether was added and the precipitated crystals were filtered off, washed with ether and dried over phosphoric anhydride in vacuum. Yield: 11.5 g (45%), colorless crystals with m. p. 104-105° (from alcohol).

Found %: C 72.65, 72.88; H 7.50, 7.55; N 5.96, 5.81. $C_{14}H_{17}O_2N$. Calculated %: C 72.70; H 7.41; N 6.06.

The compound is readily soluble in hot alcohol, less readily in cold alcohol and poorly soluble in ether.

Ethyl ester of 5-N-phenylamino-2,4-octadienoic acid (III) (R= C_3H_7). 2-Carbethoxy-5-N-phenylamino-2,4-octadienoic acid (25.0 g) was decarboxylated as described above and to the residue was added 60 ml of 30% aqueous acetic acid; the mixture was heated on a steam bath for 30 minutes, extracted with benzene, the extracts were washed with water and dried over magnesium sulfate; distillation gave 11.3 g (44%) of a substance with b.p. 171-172° (0.5 mm), $n^{20}D$ 1.5150.

Found %: N 5.17, 5.20. $C_{16}H_{21}O_2N$. Calculated %: N 5.40.

The substance was a light yellow oil which was miscible with organic solvents and insoluble in water; it was readily hydrolyzed by hydrochloric acid with formation of aniline hydrochloride.

Ethyl ester of 5-oxo-3-hexenoic acid (IV) (R= CH_3). Ethyl ester of δ-N-phenylaminosorbic acid (8.5 g) was suspended in 20 ml of water, treated with 5 ml of ether and to the mixture 4 ml of concentrated hydrochloric acid was slowly added with shaking. After dissolution of the precipitate, there was added 20 ml of water, the mixture was extracted three times with benzene, the extracts were washed with water, dried over sodium sulfate and aluminum oxide, and distilled, yielding 2.1 g (40%) of the substance with b.p. 87-88° (2 mm), d^{20}_4 1.0350, $n^{20}D$ 1.4578.

Found %: C 61.36, 61.25; H 7.81, 7.76. $C_8H_{12}O_3$. Calculated %: C 61.52; H 7.75.

The product was a colorless oil which was stable in storage and gave a cherry-red color with a solution of ferric chloride after several hours.

Ethyl ester of 5-oxo-3-octenoic acid (IV) (R= C_3H_7). 2-Carbethoxy-5-N-phenylamino-2,4-octadienoic acid (19.2 g) was heated in an oil bath to 120° until cessation of loss of carbon dioxide; after cooling 8 ml of concentrated hydrochloric acid was added to the residue, the mixture was shaken for ten minutes (aniline hydrochloride precipitated), stirred for ten minutes at 60°, diluted with water and, after treatment analogous to that described in the preceding experiment, there was formed 4.0 g (35%) of the substance with b.p. 102-103° (0.5 mm) d^{20}_4 1.0076, $n^{20}D$ 1.4538.

Found %: C 65.10, 65.17; H 8.96, 8.93. $C_{10}H_{16}O_3$. Calculated %: C 65.19; H 8.75.

The product was a colorless liquid which gave a cherry-red color with a solution of ferric chloride after several hours.

Ethyl ester of 5-oxo-3-decenoic acid (IV) ($R = C_5H_{11}$). This was prepared analogously to the preceding compound from 33.1 g of 2-carbethoxy-5-N-phenylamino-2,4-dodecanoic acid and 14 ml of concentrated hydrochloric acid. There was obtained 6.4 g (26%) of the substance with b.p. 120.5-122° (0.5 mm), d^{20}_4 0.9761, $n^{20}D$ 1.4566.

Found %: C 68.12, 68.03; H 9.56, 9.59. $C_{12}H_{20}O_3$. Calculated %: C 67.89; H 9.50.

It was a colorless oil which gave a cherry-red color with a solution of ferric chloride after several hours.

SUMMARY

1. α-Carbethoxy-δ-amino-(or arylamino)-2,4-alkadienoic acids are formed in the reaction of ammonia or aniline with 6-alkyl-3-carbethoxy-α-pyrones. This reaction is a new type of opening of the α-pyrone ring.

2. A method of synthesis of previously unknown esters of 5-oxo-3-alkenoic acids was developed, these products being vinylogs of esters of β-oxo acids which are obtained by successive decarboxylation and hydrolysis of α-carbethoxy-δ-N-arylamino-2,4-alkadienoic acids.

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SYNTHESIS OF ALIPHATIC β-CHLOROVINYL KETONES FROM HYDROXYMETHYLENE KETONES

N. K. Kochetkov, Ivan Ambrush, T. I. Ambrush and E. S. Severin

β-Chlorovinyl ketones may be employed widely in organic syntheses [1] owing to their high order of reactivity and the possibilities of their use are also determined by their availability. The most convenient method of synthesis of these compounds is the direct condensation of acyl chlorides with acetylene or vinyl chloride. usable for the preparation of aryl β-chlorovinyl ketones, alkenyl β-chlorovinyl ketones and alkyl β-chlorovinyl ketones [2-5]. Another method of their synthesis consists of the treatment of corresponding hydroxymethylene ketones with halogen compounds of phosphorus or with thionyl chloride [6, 7]; this method was used for preparative purposes in the synthesis of aryl β-chlorovinyl ketones [8]. This method has not been used to this day for the synthesis of the simplest alkyl β-chlorovinyl ketones since these are prepared more conveniently by the above-cited direct method. However, in those cases in which the direct synthesis of alkyl β-chlorovinyl ketones would be impossible for some reasons, their preparation from hydroxymethylene ketones could have a certain significance.

In the present brief communication we cite two examples of synthesis of aliphatic β-chlorovinyl ketones from hydroxymethylene ketones which show the complete applicability of this method in the aliphatic series as well.

An attempt at the direct synthesis of tert-butyl β-chlorovinyl ketone ended in failure since as the result of the condensation of the chloride of pivalic acid with acetylene in the presence of aluminum chloride we obtained a difficultly separable mixture of several substances which was, in all probability, connected with isomerization of the tertiary butyl radical under the reaction conditions. In connection with this fact we studied in detail the reaction of hydroxymethylenepinacolone, formed by formylation of pinacolone, with thionyl chloride in benzene solution. It turned out that the replacement of the enolic hydroxyl of hydroxymethylene ketone by chlorine proceeds sufficiently readily, but owing to the fact that tert-butyl β-chlorovinyl ketone and hydroxymethylenepinacolone are very difficult to separate by fractional distillation and the use of a large excess of thionyl chloride leads to side reactions, one must take for the reaction a very small excess of thionyl chloride (not over 10%) and the starting hydroxymethylene ketone must be preliminarily isolated in the individually pure state. An analogous technique was used by us for the preparation of α-methylisobutyl-β-chlorovinyl ketone, the synthesis of which by the direct method is impossible since it is well known that monoalkylacetylenes yield β-alkyl-β-chlorovinyl ketones in condensations with acyl chlorides [9]. The above compound was isolated by us by treatment of 2-hydroxymethylene-5-methyl-3-hexanone with thionyl chloride, the ketone having been prepared by the synthetic method for hydroxymethylene ketones which had been developed in our laboratory [10]. In this case, as in the previous one, the result of the reaction is determined to a large degree by the correct selection of the amount of thionyl chloride used. With strict adherence to the proper technique, yields of alkyl β-chlorovinyl ketones reach 70-75 percent and there is no doubt that if necessary this method may be used for the synthesis of other alkyl β-chlorovinyl ketones as well.

By employing methods which had been developed previously in our laboratory [1], we prepared from tert-butyl β-chlorovinyl ketone the following substances in good yields: 3-tert-butylpyrazole, ferrochloride of 2-tert-butylnaphtho(1,2:5,6)-pyrillium, as well as tert-butyl 3-pyrazolyl ketone (which was necessary for some other work being done by us [11]), while tert-butyl-β-aminovinyl ketone had been prepared by us previously [12].

These reactions indicate that tert -butyl-β -chlorovinyl ketone does not differ in its reactivity from other compounds of this class despite the presence of the bulky radical which often causes steric hindrance.

EXPERIMENTAL

Hydroxymethylenepinacolone. Into a three-necked flask, provided with a stirrer, a reflux condenser and a dropping funnel, there was placed a suspension of 10.5 g of finely powdered sodium in 250 ml of dry benzene. To this was added 35 ml of dry ethyl formate, with ice-cooling and with energetic stirring, after which 50 ml of dry pinacolone was added dropwise over 35-40 minutes. The mixture was stirred with cooling for 4-5 hours. After 2.5-3 hours the sodium salt of hydroxymethylenepinacolone began to precipitate. The thickened mixture was left overnight, after which it was carefully treated, with stirring, with 50 ml of water which was added dropwise; after having been acidified with 10% sulfuric acid, the mixture formed two layers; the aqueous layer was separated and extracted several times with ether. The benzene layer and the ethereal extract were dried over ignited magnesium sulfate and the solvents were distilled under vacuum. The residue was vacuum distilled. The yield of hydroxymethylenepinacolone was 29 g (57%). After a second distillation the substance had the following constants:

B.p. 53-56° (25 mm), $n^{20.5}_D$ 1.4523. Literature data for the hydroxymethylenepinacolone: b.p. 43.5-45° (13 mm) [13], n^{20}_D 1.4527 [14].

Tert -butyl-β -chlorovinyl ketone. To a solution of 8.2 g of hydroxymethylenepinacolone in 40 ml of absolute benzene there was added over 30 minutes, with cooling, a solution of 4.95 ml of thionyl chloride in 20 ml of anhydrous benzene. The mixture was allowed to come up to room temperature, after which it was refluxed for 8 hours, benzene was distilled off under vacuum and the residue was subjected to distillation, a fraction with b.p. 65-70° (30 mm) being collected. The yield of tert -butyl-β -chlorovinyl ketone was 6.8 g (73%). The substance had the following constants after a second distillation:

B.p. 66-67.5° (27 mm), d^{20}_4 1.0031, n^{20}_D 1.4593, MR_D 39.98; Calc. 38.94.
Found %: C 57.66, 57.50; H 7.91, 7.90. $C_7H_{11}OCl$. Calculated %: C 57.35; H 7.56.

The product was a colorless oil with a penetrating, unpleasant odor. It was miscible with organic solvents, insoluble in water and was rather stable in storage.

Isobutyl-α-methyl-β -chlorovinyl ketone. This was prepared under similar conditions from 4.18 g of 2-hydroxymethylene-5-methyl-3-hexanone and 2.3 ml of thionyl chloride in 30 ml of anhydrous benzene. After the usual treatment, a distillation gave 3.53 g (75%) of the product with b.p. 68-70° (7 mm). The substance had the following constants after a second distillation:

B.p. 68-70° (7 mm), d^{20}_4 0.9892, n^{20}_D 1.4573, MR_D 44.21; Calc. 43.55.
Found %: Cl 22.53. $C_8H_{13}OCl$. Calculated %: Cl 22.13.

The substance was a colorless liquid with a sharp, unpleasant odor; it was miscible with organic solvents and insoluble in water; it was quite stable in storage.

Tert -butyl-3-pyrazolyl ketone. To an ethereal solution of diazomethane, prepared from 5.4 g of nitrosomethylurea, a solution of 4.5 g of tert.-butyl-β -chlorovinyl ketone in 20 ml of absolute ether was added gradually with ice-cooling. The solution lost its color rapidly and after 1-2 hours there began the precipitation of crystals of tert -butyl-3-pyrazolyl ketone hydrochloride. The mixture was set aside for one day, after which the precipitated hydrochloride was filtered off and treated with a hot 15% sodium carbonate solution; the resulting tert -butyl-3-pyrazolyl ketone was then filtered off. Its yield was 2.4 g (51.5%). It formed colorless needles after recrystallization from benzene; m.p. 99-100°; the product was readily soluble in ether, alcohol and acetone; it was difficultly soluble in cold water, benzene and petroleum ether.

Found %: C 63.13, 63.05; H 7.89. 7.94. $C_8H_{12}ON_2$. Calculated %: C 63.13; H 7.95.

Its oxime was prepared in aqueous alcohol; it formed colorless crystals with m.p. 161.5-163°, after recrystallization from toluene.

Found %: N 25.64, 25.50; $C_8H_{13}ON_3$. Calculated %: N 25.13.

3(5)-Tert -butylpyrazole. To a solution of 13.7 g of tert -butyl-β-chlorovinyl ketone in 80 ml of ether there was added dropwise, but rapidly, 18.5 ml of an 80% solution of hydrazine hydrate, with cooling by tap water and with shaking. The mixture was set aside overnight, after which it was refluxed for one hour. After being cooled, the mixture was treated with 90 ml of 40% sodium hydroxide solution, the resulting aqueous layer was extracted with ether, the ethereal layer was dried over ignited potassium carbonate and the ether was distilled. The residue was vacuum distilled with the product coming over totally within the range of 135-136° (38 mm) after which it solidified on standing to a crystalline mass with m.p. 48-51°. Yield: 8.5 g (73%); b.p. 214-215° (748 mm), $n^{26.5}D$ 1.4825 (supercooled); it was readily soluble in organic solvents and difficultly soluble in water.

Found %: C 67.83, 67.92; H 10.19, 10.06. $C_7H_{12}N_2$. Calculated %: C 67.70; H 9.74.
Literature data [15]: b.p. 214° (760 mm), 115° (15 mm), m.p. 53-55.

The picrate of this substance was prepared in alcohol; it formed yellow needles with m.p. 139.5-141°, after being recrystallized from alcohol.

Found %: N 19.53, 19.98 $C_{13}H_{15}O_7N_5$. Calculated %: N 19.83,

Ferrochloride of 2-tert -butylnaphtho-(1,2:5,6)-pyrillium. To a solution of 1.36 g of β-naphthol in 14 ml of glacial acetic acid there was added 1.5 g of tert -butyl-β-chlorovinyl ketone, followed by 8 ml of a solution of of anhydrous ferric chloride in concentrated hydrochloric acid (10 g $FeCl_3$ in 15 ml of the acid). A precipitate soon began to form; the mixture was set aside for one hour, after which the precipitate was filtered off and washed on the filter with small amounts of glacial acetic acid and absolute ether. The yield of 2-tert-butylnaphtho-(1,2:5,6)-pyrillium ferrochloride was 2.5 g (56%); it formed yellow needles with m. p. 195-197.5°, after being recrystallized from glacial acetic acid; it was insoluble in organic solvents and was decomposed by water.

Found %: C 46.94, 46.84; H 4.02, 4.14. $C_{17}H_{17}OCl_4Fe$. Calculated %: C 46.94; H 3.94.

SUMMARY

It was shown that the method of synthesis of β-chlorovinyl ketones by treatment of the corresponding hydroxymethylene ketones with thionyl chloride is applicable to the aliphatic series. It is possible to prepare the previously inaccessible α-alkyl-β-chlorovinyl ketones by this method.

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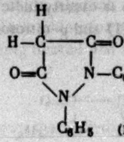
STUDIES IN THE FIELD OF CHEMISTRY OF PYRAZOLIDINE

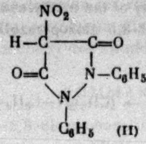
III. STUDY OF THE REACTIVITY OF 1,2-DIPHENYL-3,5-DIOXOPYRAZOLIDINE (NITRATION, SULFATION, ETC.)

A. M. Khaletskii, V. G. Pesin and Têng Jun-Hsiang

In the present paper there are given the data from a further study of the reactivity of the methylene group of 1,2-diphenyl-3,5-dioxopyrazolidine (I). In nitration of this compound by a mixture of concentrated nitric and sulfuric acids (with cooling) there is formed a mono-nitro derivative which carries the nitro group, as one may suppose, in the C_4 position (II).



(I)



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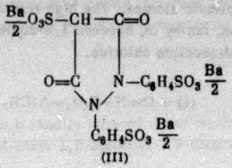
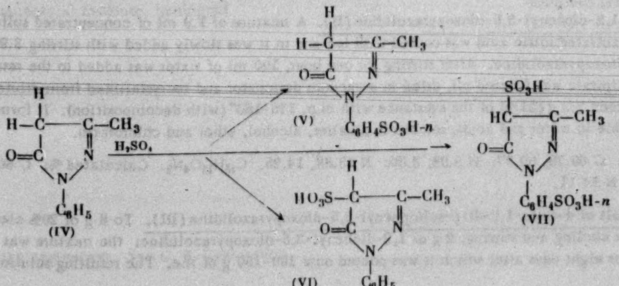
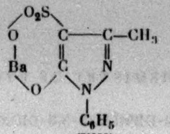


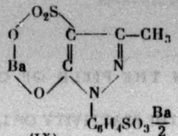
(III)

This supposition arises from the fact that the hydrogen atoms at C_4 are rather mobile [1]. In addition to this, if the nitro group had entered the benzene ring, one should have expected the formation of a dinitro derivative. The nitro derivative on being reduced with tin in the presence of hydrochloric acid is transformed into the corresponding amino derivative, which after diazotization and subsequent coupling with 2-naphthol forms a dye. However, owing to the instability of the resulting product, presumably 4-amino-1,2-diphenyl-3,5-dioxopyrazolidine, the latter cannot be isolated. Thus, the reduction product behaves itself analagous to 4-aminopyrazole. Sulfonation of 1,2-diphenyl-3,5-dioxopyrazolidine leads, judging by the analytical data for the barium salt, to the trisulfo derivative (presumably with structure III). This supposition may be made on the basis of the comparison with literature data [3] according to which the sulfonation of 1-phenyl-3-methyl-5-pyrazolone, (IV), which is close in structure, leads to (V), (VI) and also to (VII), containing the sulfo groups in C_4 position in the



pyrazolone nucleus and in para-position in the benzene nucleus. The authors investigated some properties of the cited sulfonic acids, specifically the reactions of the latter with nitrous acid and with aryl diazonium salts. The data obtained by them permitted them to assign structures (VIII) amd (IX) to the barium salts of the sulfonic (VI) and disulfonic acids (VII).

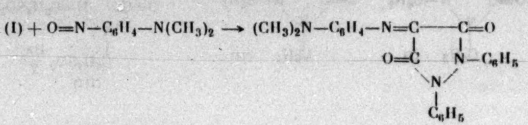

(VIII)

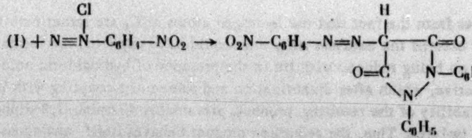

(IX)

In checking these data [2] in respect to the sulfonation product of 1,2-diphenyl-3,5-dioxopyrazolidine we also observed approximately the same phenomenon and, therefore, structure (III) for the sulfonation product of 1,2-diphenyl-3,5-dioxopyrazolidine is not excluded.

Thus, in nitration and sulfonation the pyrazolidine ring behaves like the pyrazolone ring, at it does in halogenation and thiocyanation [1].

In a comparison of the reactivity of the pyrazolidine ring with the analogous ability of typical aromatic compounds (benzene, aromatic amines) one may conclude that the 3,5-dioxopyrazolidine ring comes close in properties to the aromatic amines. The high reactivity of the methylene group is clearly indicated by the reactions of condensation, run by us, between 1,2-diphenyl-3,5-dioxopyrazolidine (I) and p-nitrosodimethylaniline and p-nitrobenzenediazonium chloride.





The totality of the data thus obtained indicates, therefore, the high mobility of the hydrogen atoms in the methylene group of 1,2-diphenyl-3,5-dioxopyrazolidine.

EXPERIMENTAL

4-Nitro-1,2-diphenyl-3,5-dioxopyrazolidine (II). A mixture of 1.9 ml of concentrated sulfuric acid and 1.5 ml of concentrated nitric acid was cooled with ice and to it was slowly added with stirring 3.9 g of 1,2-diphenyl-3,5-dioxopyrazolidine. After stirring for one hour, 100 ml of water was added to the resulting thick mass; the precipitate was filtered off, dried in a vacuum desiccator and recrystallized from dilute alcohol; there was obtained 2.3 g (51%) of the substance with m.p. 175-180° (with decomposition). It formed dark yellow crystals, insoluble in water and acids, soluble in alkalies, alcohol, ether and chloroform.

Found %: C 60.79, 60.87; H 3.98, 3.50; N 13.88, 14.25. $C_{15}H_{11}O_4N_3$. Calculated %: C 60.61; H 3.70; N 14.11.

Barium salt of 4-sulfo-1,2-di-p-sulfophenyl-3,5-dioxopyrazolidine (III). To 8 g of 20% oleum there was added, with ice cooling and stirring, 2 g of 1,2-diphenyl-3,5-dioxopyrazolidine; the mixture was left in a closed vessel for eight days after which it was poured onto 100-150 g of ice. The resulting solution was neutralized to Congo red with barium carbonate, the precipitated barium sulfate was filtered off and washed with hot water, and to the combined filtrate there was added dropwise enough ethyl alcohol to produce turbidity. After cooling, there separated a fine crystalline precipitate which, after being washed with alcohol, was dried in air; there was obtained 2.1 g of the substance (72%).

Found %: Ba 27.96, 26.85. $C_{15}H_9O_{11}N_2S_3Ba_{1.5}\cdot 3H_2O$. Calculated %: Ba 27.43.

Product of condensation of p-dimethylaminonitrosobenzene with 1,2-diphenyl-3,5-dioxopyrazolidine. A mixture of 4 g of 1,2-diphenyl-3,5-dioxopyrazolidine, 2.4 g of p-nitrosodimethylaminobenzene and 30 ml of alcohol was stirred at 20-30°, the resulting precipitate was filtered off, washed with ether, dried, dissolved in chloroform and boiled with charcoal. After addition of ether to the chloroform filtrate, the separated precipitate was filtered off and washed with a mixture of chloroform and ether; there was obtained 3 g (50%) of the substance with m.p. 210-215°. It formed a deep violet powder, insoluble in water, ether, alkalies and acids, but soluble in alcohol and chloroform.

Found %: C 71.68, 71.42; H 5.35, 5.25; N 13.61, 13.48. $C_{23}H_{20}O_2N_4$. Calculated %: C 71.87; H 5.21; N 14.58.

Product of azo coupling of 1,2-diphenyl-3,5-dioxopyrazolidine with p-nitrobenzenediazonium chloride. To an aqueous solution of 2 g of the sodium derivative of 1,2-diphenyl-3,5-dioxopyrazolidine there was slowly added, with ice cooling, a solution of p-nitrobenzenediazonium chloride, prepared from 1.4 g of 4-nitroaniline. The precipitated orange product was filtered off, washed with water and, after being dried in air, was recrystallized from chloroform; there was obtained 2.6 g of it (80%) with m.p. 271-272°. It formed orange crystals, insoluble in water, acids, alcohol, benzene, acetone and ether, sparingly soluble in carbon tetrachloride and more readily soluble in chloroform; it was insoluble in dilute solution of sodium hydroxide in the cold, but does dissolve in it on being heated and forms a cherry-red solution.

SUMMARY

1. It was shown that 1,2-diphenyl-3,5-dioxopyrazolidine is readily nitrated under conditions which are usual for aromatic compounds with formation, most likely, of 4-nitro-1,2-diphenyl-3,5-dioxopyrazolidine.

2. It was shown that 1,2-diphenyl-3,5-dioxopyrazolidine is sulfonated by oleum with formation of, presumably, a trisulfo derivative – 4-sulfo-1,2-di-p-sulfophenyl-3,5-dioxopyrazolidine.

3. It was found that 1,2-diphenyl-3,5-dioxopyrazolidine readily reacts with p-nitrosodimethylaniline and benzenediazonium chloride with formation of the corresponding products of condensation at the hydrogens of the methylene group.

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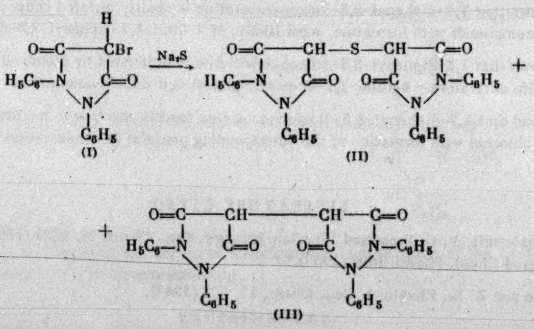
**In Russian.

STUDIES IN THE FIELD OF CHEMISTRY OF PYRAZOLIDINE

IV. SYNTHESIS AND STUDY OF SULFIDES AND DISULFIDES OF 1,2-DIPHENYL-AND 4-n-BUTYL-1,2-DIPHENYL-3,5-DIOXOPYRAZOLIDINES

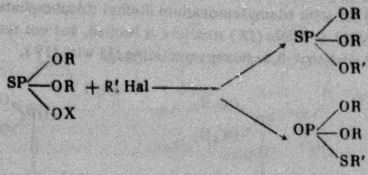
V. G. Pesin, A. M. Khaletskii and Têng Jun-Hsiang

It was recently shown by us [1, 2] that hydrogen atoms of the methylene group of 1,2-diphenyl-3,5-dioxopyrazolidine readily react in substitution reactions. In the present paper there are described some data on the study of the reactivity of chloro-, bromo- and thiocyano-derivatives of 1,2-diphenyl- and 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidines. 4-Bromo-1,2-diphenyl-3,5-dioxopyrazolidine (I) readily reacts with sodium sulfide with predominant formation of sulfide (II); as a byproduct there is formed bis-(1,2-diphenyl-3,5-dioxopyrazolidine) (III), the structure of which is proved by an alternate synthesis (by the reaction of bis-malonic ester with hydrazobenzene).



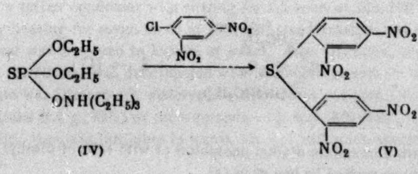
The great mobility of the halogen in compound (I) and the aromatic character of the pyrazolidine ring, disclosed by us previously in reactions of nitration, sulfonation, halogenation and thiocyanation, permits a comparison of (I) with 2,4-dinitrochlorobenzene, in which, as it is known, the aromatic properties and the high reactivity of the halogen are combined. In view of this, we also examined the reaction of (I) with triethylammonium diethyl thiophosphate (IV).

As it is known, alkali salts of dialkyl thiophosphates have a dual reactivity. Thus, for example, in the reaction with halogen derivatives of the aliphatic series they form two series of derivatives: esters with the thiono and the thiolo structure [3]:



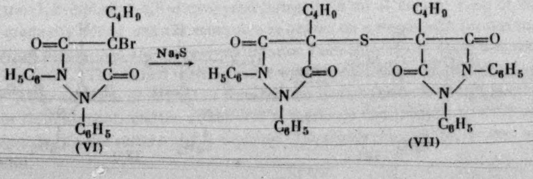
X – cation; Hal – halogen; R – alkyl; R' – alkyl, aralkyl or acyl.

As to the reactions of the salts of dialkyl thiophosphates with aromatic halogen derivatives, no data exist on them in the literature. As it was shown by one of us [4], the sodium, ammonium and triethylammonium salts of diethyl dithiophosphate react with 2,4-dinitrochlorobenzene with formation of 2,4,2',4'-tetranitrodiphenyl sulfide (V).



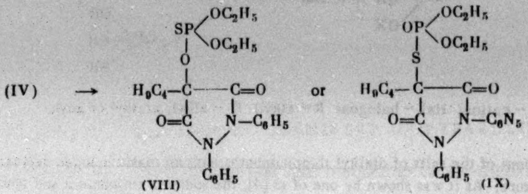
In a further study of the given reaction it was found that the latter proceeds analogously with other aromatic and heterocyclic halogen derivatives. It was shown by us that 4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine (I) reacts with triethylammonium diethyl thiophosphate (IV) analogously to the reaction of the latter with 2,4-dinitrochlorobenzene with formation of sulfide (II); as a byproduct in this case, as in the reaction with sodium sulfide, there is formed bis-(1,2-diphenyl-3,5-dioxopyrazolidine) (III). The indicated analogy of properties of 2,4-dinitrochlorobenzene and 4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine (I) permits one to suppose that the activating influence of the carbonyl groups in (I) in respect to the reactivity of the halogen at C_4 position in the latter is approximately the same as that of the two nitro groups in 2,4-dinitrochlorobenzene.

In order to study the effect of an alkyl group at C_4 on the mobility of the halogen, we studied the reaction of 4-bromo-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine (VI) with sodium sulfide; it was shown that in this reaction the corresponding sulfide (VII) is also formed.

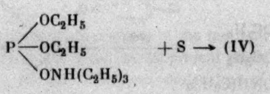


However, in this case we failed to isolate, along with the main product, any of the sulfur-free products of condensation of two pyrazolidine rings (III) as was the case in the reaction of 1,2-diphenyl-3,5-dioxopyrazolidine with sodium sulfide, which in fact may be explained by the blocking effect of the butyl radical on the mobility of the halogen.

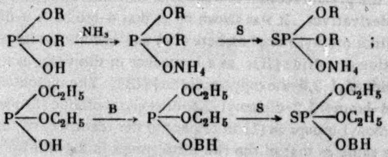
The notable effect of the butyl radical is also observed in the reaction of 4-bromo-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine (VI) with triethylammonium diethyl thiophosphate (IV). In this reaction the corresponding ester of thione (VIII) or thiolo (IX) structure is formed, but not the sulfide (VII), as is the case in the reaction of 4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine (I) with (IV).


(VIII) (IX)

The starting triethylammonium diethyl thiophosphate was prepared by us by addition of sulfur to triethylammonium diethyl phosphite

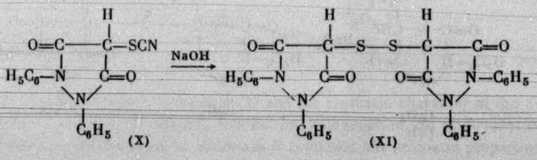


by the reaction of sulfur with ammonium dialkyl phosphites or with salts of diethyl phosphorous acid and organic bases, a reaction that had been studied by one of us [4].



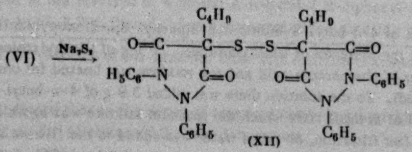
B — various primary, secondary or tertiary organic bases

4-Thiocyano-1,2-diphenyl-3,5-dioxopyrazolidine (X) reacts readily with alcoholic alkali with formation of the di-sulfide (XI).


(X) (XI)

We failed to isolate the corresponding disulfide in running this reaction with 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine; in this case we isolated a substance which was free of sulfur and had the composition of (in %): C 73.34, H 7.20, N 11.55, which was not studied further.

Disulfide (XII) was prepared by the reaction of 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine (VI) with sodium disulfide.



(XII)

The data from the study of the reactions of bromo- and thiocyano-derivatives of 1,2-diphenyl-3,5-dioxopyrazolidine and its C_4-n-butyl derivative with sodium sulfide and disulfide, with triethylammonium diethyl thiophosphate and with alcoholic alkali, show sufficiently clearly that in these reactions the n-butyl radical at C_4 position causes a material and evidently hindering effect on the direction of the process.

EXPERIMENTAL

4,4-Bis-(1,2-diphenyl-3,5-dioxopyrazolidine)(III). Heating 0.83 g of metallic sodium in 50 ml of anhydrous alcohol, 5.7 g of bis-malonic ester prepared by method [5], and 7.7 g of hydrazobenzene on an oil bath in a flask provided with a reflux condenser with stirring for 1.5 hours at 120-130° was followed, after distillation of the alcohol, by heating for seven hours at 150-160° (tar formation was observed at above 165°); after being cooled, the mixture was dissolved in 150 ml of water. After filtration, the alkaline aqueous solution was extracted with ether and the filtrate was decomposed with hydrochloric acid (to acid reaction with Congo red). The resulting precipitate was filtered off, dissolved in chloroform and precipitated from the hot solution with alcohol; there was obtained 6.4 g (72%) of the substance with m.p. 240-242°. It forms colorless small needles which turn pink in air; they are insoluble in water, alcohol and acids, sparingly soluble in ether and readily soluble in chloroform.

Found %: C 71.62, 71.84; H 4.68, 4.40; N 11.29, 11.25. $C_{30}H_{22}O_4N_4$. Calculated %: C 71.71; H 4.38; N 11.16.

Sulfide of 1,2-diphenyl-3,5-dioxopyrazolidine (II). a) One g of triethylamine, 320 mg of purified sulfur and 1.38 g of diethyl ester of phosphorous acid were heated for one hour at 60-70°, during which time almost all the sulfur dissolved. After addition of 3.3 g of 4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine in 20 ml of alcohol, the reaction mixture was again heated on a water bath for five hours. The resulting precipitate was separated, washed with alcohol and recrystallized from a mixture of chloroform and alcohol; there was obtained 1 g of the substance which gave no depression in a mixed melting point with (III). After addition of 15 ml of water to the filtrate, there separated a precipitate which, after many recrystallizations from alcohol, melted at 167-173°; yield: 40%.

Found %: C 67.60, 67.37; H 4.52, 4.17; N 10.35, 10.91. $C_{30}H_{22}O_4N_4S$. Calculated %: C 67.42; H 4.12; N 10.49.

To 3 g of 4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine in 20 ml of alcohol 0.6 g of sodium sulfide in 15 ml of alcohol was gradually added and the mixture was heated on a steam bath for two hours. After the separation of the resulting precipitate and its recrystallization from chloroform, there was obtained 0.8 g (33%) of product with m.p. 240-242°. The mixed melting point with bis-(1,2-diphenyl-3,5-dioxopyrazolidine) (III) showed no depression. After addition of 300 ml of water to the filtrate, there formed a precipitate which, after many recrystallizations from alcohol, melted at 165-170°; there was obtained 1.1 g (42%) of the product which in its properties corresponded to the sulfide of 1,2-diphenyl-3,5-dioxopyrazolidine. Mixed melting point with the latter gave no depression.

Sulfide of 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine (VII). To a solution of 2.88 g of 4-bromo-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine in 15 ml of alcohol there was added, with constant stirring, an alcoholic solution containing 0.48 g of sodium sulfide, after which the reaction mixture was heated for two hours on a steam bath. After addition of 20 ml of water to the filtrate, the resulting precipitate was combined with the original precipitate, obtained above, and the total was recrystallized from alcohol; there was formed 1.5 g (62.5%) of the product with m.p. 67-70°.

Found %: C 70.34, 70.72; H 5.82, 6.12; N 8.87, 8.47. $C_{38}H_{38}O_4N_4S$. Calculated %: C 70.74, H 5.88; N 8.67.

A study of the reaction of 4-n-butyl-4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine with sulfur and diethyl ester of phosphorous acid (in the presence of triethylamine). To 1 g of triethylamine there was added 320 mg of sulfur, sulfur, 1.38 g of diethyl ester of phosphorous acid and the mixture was heated for one hour at 60° (whereupon almost all the sulfur dissolved). To the solution there was added 3.9 g of 4-n-butyl-4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine and 20 ml of alcohol after which the reaction mixture was again subjected to heating on a water bath for five hours. After filtration, 50 ml of water was added to the filtrate and the resulting precipitate was subjected to recrystallization from alcohol; there was obtained 3.1 g (65%) of the product with m.p. 92.5-93.5°.

Found %: C 58.74, 58.33; H 6.28, 6.45; N 6.26, 6.25; S 6.41, 6.12. $C_{23}H_{29}O_5N_2SP$. Calculated %: C 57.98; H 6.09; N 5.88; S 6.72.

Disulfide of bis-(1,2-diphenyl-3,5-dioxopyrazolidine) (XI). 4-Thiocyano-1,2-diphenyl-3,5-dioxothiazolidine (1.5 g) was heated to boiling in 15 ml of alcohol, after which 0.2 g of sodium hydroxide was added. The resulting yellow precipitate was filtered off after one hour of heating and was recrystallized from alcohol; there was obtained 1.4 g (50.9%) of the product with m.p. 265-269° (with decomposition). It forms bright yellow crystals, soluble in water; on acidification of the solution a colorless precipitate formed.

Found %: C 63.48. 63.33; H 3.93, 3.74; N 10.38, 9.95. $C_{30}H_{22}O_4N_4S_2$. Calculated %: C 63.60; H 3.89; N 9.89.

Disulfide of di-(4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine)(XII). Sodium sulfide (1.6 g) was dissolved in 10 ml of 95% alcohol with heating, 0.2 g of powdered sulfur was added to the solution and heating was continued until the sulfur dissolved completely. Then the solution was added to 3 g of 4-bromo-4-butyl-1,2-diphenyl-3,5-dioxopyrazolidine in 10 ml of alcohol and, after being heated on a water bath for three hours, the reaction mixture was subjected to filtration. After addition of 60 ml of water, the resulting precipitate was filtered off and recrystallized from alcohol. There was obtained 1.04 g (40%) of the product with m.p. 153-155°.

Found %: N 7.72, 8.12; S 9.81, 9.83. $C_{38}H_{38}O_4N_4S_2$. Calculated %: N 8.23; S 9.44.

A study of the reaction of 4-thiocyano-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine with sodium hydroxide. To a solution of 1.5 g of 4-thiocyano-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine in 15 ml of alcohol there was added a solution of 0.2 g of sodium hydroxide in 10 ml of alcohol and the reaction mixture was refluxed for two hours. After cooling and filtration, the solution was evaporated to dryness on a water bath, the residue was taken up in water and the aqueous solution was extracted with ether to remove the impurities. After acidification of the aqueous filtrate with hydrochloric acid, a precipitate formed, which after recrystallization from alcohol, melted at 102-103°; there was obtained 1.2 g of the substance. It formed colorless small needles which were sulfur-free, and were insoluble in alkalies and acids, but soluble in water, alcohol, ether and chloroform.

Found %: C 73.33, 73.34; H 7.30, 7.15; N 11.38, 11.78.

SUMMARY

1. It was found that 4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine reacts both with sodium sulfide and with triethylammonium diethyl thiophosphate, with formation, as the main product, of di-(1,2-diphenyl-3,5-dioxopyrazolidine) sulfide and of bis-(1,2-diphenyl-3,5-dioxopyrazolidine) as a byproduct.

2. It was found that 4-bromo-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine reacts both with sodium sulfide with formation of bis-(4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine) sulfide and with triethylammonium diethyl thiophosphate, with formation of 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine thiophosphate with thiono or thiolo structure.

3. It was established that 4-thiocyano-1,2-diphenyl-3,5-dioxopyrazolidine reacts readily with alcoholic alkali, forming di-(1,2-diphenyl-3,5-dioxopyrazolidine) disulfide, while in the reaction of 4-thiocyano-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine with alcoholic alkali the reaction product is a sulfur-free substance.

4. It was established that in the reaction of 4-bromo-4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine with sodium disulfide di-(4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidine) disulfide is formed.

5. It was shown that in the reaction of bis-malonic ester with hydriazobenzene bis-(1,2-diphenyl-3,5-dioxopyrazolidine is formed.

6. Experimental data indicate that in the series of reactions the n-butyl group in C_4 position displays a predominantly blocking effect on the direction of the reaction process.

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CHEMISTRY OF SELENOPHENE

XIII. CYANOETHYLATION OF KETONES OF THE SELENOPHENE SERIES

Iu. K. Iur'ev, N. K. Sadovaia and V. V. Titov

In one of our previous papers [1] we reported on the aminomethylation of ketones of the selenophene series, by means of the Mannich reaction, in which we prepared a series of β-dimethylaminoalkyl 2-selenienyl ketones.

In the present work, in continuing the study of the reactivity of ketones of this series, we examined the possibility of cyanoethylation of these substances. It is known from the literature that cyanoethylation of the simplest ketones of furan and thiophene series – 2-acylfurans and 2-acylthiophenes – proceeds with a quantitative yield in the presence of "Triton B"; in running the reaction in the presence of alkali the cyanoethylated ketones are also formed but in lower yields, which do not rise above 50% [2-4]. In the work by Acara and Levine [5], devoted to cyanoethylation of ketones of furan and thiophene series with a more complex structure, run also in the presence of "Triton B", it was noted that 2,5-dimethyl-3-acetofuran forms even under the most favorable conditions, only a low yield of the tricyanoethyl derivative (15.7%); as to 2,5-dimethyl-3-butyrofuran, during its cyanoethylation there was formed only the monocyanoethyl derivative in 54.3% yield, instead of a di-cyanoethyl derivative.

In the present work we took for the cyanoethylation reaction not only the simplest ketones of the selenophene series, such as methyl, ethyl and isopropyl 2-selenienyl ketones, but also those with more complex structure, containing a methyl group in ortho-position in respect to the acyl group, as for example: methyl 3-methyl-2-selenienyl ketone, isopropyl 3,4-dimethyl-2-selenienyl ketone and isopropyl 3,5-dimethyl-2-selenienyl ketone.

These ketones were prepared by the method described by us in our previous papers – by acylation of selenophene and its homologs with silicoanhydrides of the corresponding monobasic acids in the presence of anhydrous stannic chloride [6, 7], while in the case of acylation of selenophene and dimethylselenophene with the silicoanhydride of isobutyric acid the yields of the respective ketones were 45-61% and only in the case of acylation of 3-methylselenophene was the yield as low as 33.5%.

Cyanoethylation of the indicated ketones in the selenophene series was run in the medium of anhydrous tert -butyl alcohol in the presence of an alcoholic solution of potassium hydroxide. We established that by using, for the catalyst, a six-fold amount of alcoholic alkali (in comparison with the amount indicated for the cyanoethylation of the corresponding ketones of the thiophene series [2]), it is possible to prepare δ-oxonitriles of the selenophene series in yields which exceed those of the corresponding oxonitriles of the furan and thiophene series, even in case of their preparation in the presence of "Triton B".

Thus, by cyanoethylating 2-aceto-, 2-propio- and 2-isobutyroselenophene we prepared the corresponding 1', 1', 1'-tris-(cyanoethyl)-2-acetoselenophene, 1',1'-bis-(cyanoethyl)-2-propioselenophene and 1'-methyl-1'-cyanoethyl-2-propioselenophene.

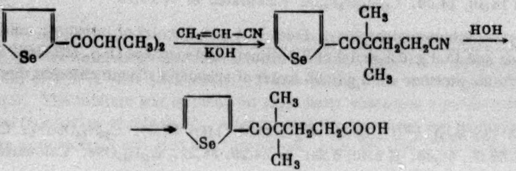
During the cyanoethylation of 3-methyl-2-acetoselenophene there was formed a noncrystallizing reaction product, the hydrolysis of which with aqueous alkali yielded 3-methyl-1', 1', 1'-tris-(carboxyethyl)-2-acetoselenophene, which proved the possibility of cyanoethylation of 3-methyl-2-acetoselenophene by a normal scheme, i. e., with formation of 3-methyl-1',1',1'-tris-(cyanoethyl)-2-acetoselenophene. However, this reaction proceeded with formation of but a small amount of the tricyanoethyl derivative of the ketone, i. e., it was just as hindered as was the case of cyanoethylation of 2,5-dimethyl-3-acetofuran, described in the literature [5].

An attempt to realize the cyanoethylation of ketones of the selenophene series which contain a methyl group in position 3 and an acyl group in position 2, the latter group having a branched radical, i. e., compounds such as 3-methyl-2-isobutyroselenophene and 3,5-dimethyl- and 3,4-dimethyl-2-isobutyroselenophene, failed to give a positive result even after heating of the reaction mixture and the use of rigorously purified reagents: the reaction failed to take place completely and the ketones were recovered in unchanged state.

The weak course of the reaction of cyanoethylation for 3-methyl-2-acetoselenophene and its total absence in applications to 3-methyl-, 3,5-dimethyl- and 3,4-dimethyl-2-isobutyroselenophenes, like the literature-described preparation of only the monocyanoethyl derivative from 2,5-dimethyl-3-butyrofuran, is evidently caused by steric hindrance [5], produced by the presence of the methyl group in ortho-position in respect to the acyl group (chain branching in β-position in respect to the carbonyl group).

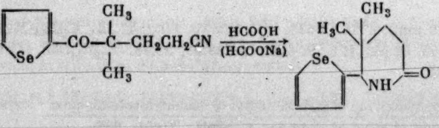
δ-Oxonitriles of the selenophene series failed to form semicarbazones or 2,4-dinitrophenylhydrazones under the usual conditions of preparation of these derivatives.

By hydrolysis of the δ-oxonitriles, synthesized by us in the selenophene series, we prepared the corresponding mono-, di- and tricarboxylic δ-oxo acids of the selenophene series, as for example:



In this way we prepared 1'-methyl-1'-carboxyethyl-2-propioselenophene, 1',1'-bis-(carboxyethyl)-2-propioselenophene. 1',1',1'-tris-(carboxyethyl)-2-acetoselenophene and 3-methyl-1',1',1'-tris-(carboxyethyl)-2-acetoselenophene.

We prepared 3,3-dimethyl-2-(2-selenienyl)-6-piperidone by reduction of 1'-methyl-1'-cyanoethyl-2-propioselenophene with anhydrous formic acid in the presence of sodium formate, by the technique which was described by A. N. Kost and his co-workers [8].



EXPERIMENTAL

1. Synthesis of ketones of selenophene series was accomplished by the method which was described by us previously [6, 7].

2-Acetoselenophene. From 3.6 g (0.06 mole) of acetic acid, 3.4 g (0.02 mole) of silicon tetrachloride and 3.9 g (0.03 mole) of selenophene in the presence of 3.9 g (0,015 mole) of stannic chloride there was obtained 3.2 g (61.5%) of the ketone.

B.p. 103-104° (10 mm), $n^{20}D$ 1.5908, d^{20}_4 1.5460, MR_D 37.82. $C_6H_6OSeF_2$. Calculated %: 37.39. Literature data: b.p. 103° (12 mm), $n^{18}D$ 1.601, d^{25}_4 1.5530 [9]; b.p. 105-106° (12 mm), $n^{20}D$ 1.5920, d^{20}_4 1.5444 [10].

2-Isobutyroselenophene. From 16 g (0.18 mole) of isobutyric acid, 10.2 g (0.06 mole) of silicon tetrachloride and 10.5 g (0.08 mole) of selenophene in the presence of 11.7 g (0.045 mole) of anhydrous stannic chloride there was obtained 9.9 g (61.5%) of the ketone.

B.p. 109-109.5° (8 mm), $n^{20}D$ 1.5680, d^{20}_4 1.3855, MR_D 47.49. $C_8H_{10}OSeF_2$. Calculated: 46.62. Found %: C 47.71, 47.75; H 5.31, 5.16; Se 38.85, 38.91. $C_8H_{10}OSe$. Calculated %: C 47.76; H 5.01; Se 39.26.

2,4-Dinitrophenylhydrazone of 2-isobutyroselenophene – crystals of cherry red color; m.p. 149.5-150° (from a mixture of alcohol and ethyl acetate). Yield: 84%.

Found %: N 14.55, 14.64; Se 20.65, 20.67. $C_{14}H_{14}O_4N_4Se$. Calculated %: N 14.70; Se 20.71.

3-Methyl-2-isobutyroselenophene. From 16.2 g (0.18 mole) of isobutyric acid, 10.2 g (0.06 mole) of silicon tetrachloride and 13.1 g (0.09 mole) of 3-methylselenophene (b.p. 137.5° at 751 mm, $n^{20}D$ 1.5615, d^{20}_4 1.4623, MR_D 32.15; calculated 32.76)* in the presence of 11.7 g of anhydrous stannic chloride (0.045 mole) there was obtained 6.5 g (33.5%) of the ketone.

B.p. 122-123° (13 mm), $n^{20}D$ 1.5578, d^{20}_4 1.3135, MR_D 52.79. $C_9H_{12}OSeF_2$. Calculated: 51.25. Found %: C 50.94, 50.74; H 6.00, 5.94. $C_9H_{12}OSe$. Calculated %: C 50.25; H 5.58.

2,4-Dinitrophenylhydrazone of 3-methyl-2-isobutyroselenophene – crystals of dark red color; m.p. 146-147° (from a mixture of ethyl acetate and alcohol). Yield: 71%.

Found %: N 14.19, 14.09. $C_{15}H_{16}O_4N_4Se$. Calculated %: N 14.18.

3,4-Dimethyl-2-isobutyroselenophene. From 17.6 g (0.2 mole) of isobutyric acid, 12 g (0.07 mole) of silicon tetrachloride and 15.9 g (0.1 mole) of 3,4-dimethylselenophene (b.p. 167-168° at 752 mm, $n^{20}D$ 1.5549, d^{20}_4 1.3957) [11] in the presence of 13 g (0.05 mole) of anhydrous stannic chloride there was obtained 10 g (44%) of the ketone.

B.p. 134-135° (13 mm), $n^{20}D$ 1.5628, d^{20}_4 1.3034. MR_D 57.00. $C_{10}H_{14}OSeF_2$. Calculated: 55.87. Found %: C 52.50, 52.48; H 6.40, 6.20; Se 34.29, 34.21. $C_{10}H_{14}OSe$. Calculated %: C 52.41; H 6.16; Se 34.45.

2,4-Dinitrophenylhydrazone of 3,4-dimethyl-2-isobutyroselenophene – crystals with red color; m.p. 206-207° (from a mixture of ethyl acetate and alcohol). Yield: 79%.

Found %: Se 19.33, 19.37. $C_{16}H_{18}O_4N_4Se$. Calculated %: Se 19.29.

3,5-Dimethyl-2-isobutyroselenophene. From 11.7 g (0.13 mole) of isobutyric acid, 9.4 g (0.055 mole) of silicon tetrachloride and 10.6 g (0.067 mole) of 2,4-dimethylselenophene (b.p. 159-160° at 750 mm, $n^{20}D$ 1.5502, d^{20}_4 1.3664) [12] in the presence of 10.4 g (0.04 mole) of anhydrous stannic chloride there was obtained 7.2 g (47.5%) of the ketone.

B.p. 120-121° (10 mm), $n^{20}D$ 1.5617, d^{20}_4 1.2877, MR_D 57.75. $C_{10}H_{14}OSeF_2$. Calculated: 55.87. Found %: C 52.53, 52.51; H 6.29, 6.32; Se 33.95, 33.98. $C_{10}H_{14}OSe$. Calculated %: C 52.41; H 6.16; Se 34.45.

2,4-Dinitrophenylhydrazone of 3,5-dimethyl-2-isobutyroselenophene – crystals of dark red color; m.p. 175-176° (from a mixture of ethyl acetate and alcohol), Yield: 62%.

Found %: Se 19.15, 19.11. $C_{16}H_{18}O_4N_4Se$. Calculated %: Se 19.29.

2. Cyanoethylation of ketones of selenophene series. 1',1',1'-Tris-(cyanoethyl)-2-acetoselenophene. Into a four necked flask with a stirrer, a dropping funnel, a thermometer and a reflux condenser we placed a solution of 1.73 g (0.01 mole) of 2-acetoselenophene in 5 ml of anhydrous tert-butyl alcohol and to this was added 0.6 ml of a saturated alcoholic solution of potassium hydroxide. Then, over a 5 minute period 3 g (0.55 mole) of acrylonitrile was added dropwise, whereupon the mixture warmed up to 40-60°. After completion of the reaction, the mixture was stirred for two hours at room temperature and was then acidified with 2 N hydrochloric acid. The color of the solution changed from dark cherry red to yellow and crystals of the tricyanoethyl derivative of 2-acetoselenophene precipitated; m.p. 138-139° (from isobutyl alcohol). Yield: 3.3 g (quantitative).

Found %: C 54.63, 54.80; H 4.71, 4.74. $C_{15}H_{15}ON_3Se$. Calculated %: C 54.22; H 4.55.

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* The constants of 3-methylselenophene are cited after distillation through a column with effectiveness of 18 theoretical plates.

1',1'-Di-(cyanoethyl)-2-propioselenophene. From 0.6 g (0.003 mole) of 2-propioselenophene (b.p. 110-111° at 10 mm, n^{20}D 1.5848) [6] and 1.2 g (0.023 mole) of acrylonitrile, in the presence of 0.25 ml of saturated alcoholic solution of potassium hydroxide, there was obtained 0.9 g (quantitative yield) of the dicyanoethyl derivative of 2-propioselenophene; m.p. 91-91.5° (from dilute alcohol).

Found %: C 53.42, 53.40; H 5.09, 4.95; Se 26.43, 26.30. $C_{13}H_{14}ON_2Se$. Calculated %: C 53.25; H 4.80; Se 26.84.

1'-Methyl-1'-cyanoethyl-2-propioselenophene. From 15 g (0.075 mole) of 2-isobutyroselenophene, 15 g (0.28 mole) of acrylonitrile, in the presence of 5 ml of saturated alcoholic solution of potassium hydroxide, there was obtained 19 g (quantitative yield) of monocyanoethyl derivative of 2-isobutyroselenophene; m.p. 93-93.5° (from dilute alcohol).

Found %: C 52.12, 52.00; H 4.50, 4.41. $C_{11}H_{13}ONSe$. Calculated %: C 51.97; H 5.12.

3-Methyl-1',1'-tris-(cyanoethyl)-2-acetoselenophene. From 2.6 g (0.014 mole) of 3-methyl-2-acetoselenophene (b.p. 119-120° at 20 mm, n^{20}D 1.5927) [1], 5 g (0.09 mole) acrylonitrile and 0.8 ml of saturated alcoholic solution of potassium hydroxide there was obtained 4.2 g of an oily reaction product which decomposed during attempted distillation in vacuum and evolved selenium; owing to this, it was subjected to hydrolysis (see below) in the crude form.

3. Preparation of δ-oxo acids of the selenophene series by hydrolysis of cyanoethylated 2-acylselenophenes.

1'1'1'-Tris-(carboxyethyl)-2-acetoselenophene. Into a round bottomed flask with a reflux condenser there was placed 0.78 g (0.002 mole) of 1',1',1'-tris-(cyanoethyl)-2-acetoselenophene and 0.6 g (0.015 mole) of sodium hydroxide in 7 ml of water. The mixture was refluxed for eight hours whereupon a partial destruction of the selenophene ring occurred (formation of selenium). After cooling the mixture it was neutralized with 2 N hydrochloric acid and the preicipitated oxo aicd was filtered off; m.p. 165-165.5° (from water). Yield: 0.48 g (52.5%).

Found %: C 46.22, 46.42; H 5.04, 5.12. M 392.2, 391.4 by titration with sodium hydroxide. $C_{15}H_{18}O_7Se$. Calculated %: C 46.28; H 4.66; M 389.2.

1',1'-Bis-(carboxyethyl)-2-propioselenophene. From 1 g (0.003 mole) of 1'1'-bis-(cyanoethyl)-2-propioselenophene by boiling with 0.5 g (0.012 mole) of sodium hydroxide in 15 ml of water there was obtained 0.9 g (78%) of the oxo acid; m.p. 130-131° (from water).

Found %: C 47.03, 46.96; H 4.98, 4.82; Se 23.71, 23.93. M 332.9, 332.4. $C_{13}H_{16}O_5Se$. Calculated %: C 47.13; H 4.84; Se 23.84; M 331.2.

1'-Methyl-1'-carboxyethyl-2-propioselenophene. From 2.54 g (0.01 mole) of 1'-methyl-1'-cyanoethyl-2-propioselenophene by refluxing with 0.9 g (0.022 mole) of sodium hydroxide in 30 ml of water there was obtained 1.5 g (53%) of the oxo acid with m.p. 83.5-84° (from water).

Found %: C 48.33, 48.33; H 5.25, 5.38; M 272.2, 272.4. $C_{11}H_{14}O_3Se$. Calculated %: C 48.35; H 5.17; M 273.2.

3-Methyl-1',1',1'-tris-(carboxyethyl)-2-acetoselenophene. From 1.1 g (0.033 mole) of crude 3-methyl-1',1',1'-tris-(cyanoethyl)-2-acetoselenophene by refluxing with 0.6 g (0.015 mole) of sodium hydroxide in 15 ml of water there was obtained 0.25 g (18.5%) of the oxo acid; m.p. 179-180° (from water).

Found %: 47.53, 47.37; H 5.24, 5.24. $C_{16}H_{20}O_7Se$. Calculated %: C 47.67; H 5.00.

3,3-Dimethyl-2-(2'-selenienyl)-6-piperidone. Into a round bottomed flask there was placed 3.8 g (0.015 mole) of 1'-methyl-1'-cyanoethyl-2-propioselenophene, 3.4 g (0.075 mole) of anhydrous formic acid and 5.1 g (0.075 mole) of sodium formate. The mixture was refluxed for 40 hours, treated with 7.8 g (0.15 mole) of formic acid and refluxed for 30 hours longer. After cooling, the mixture was diluted with 50 ml of water, made strongly alkaline, the resulting colorless crystals were separated and after washing with water, were dried; m.p. 159-160° (from ligroine). Yield: 2.6 g (68.5%).

Found %: C 51.90, 51.95; H 5.95, 5.99; Se 30.69, 30.62. $C_{11}H_{15}ONSe$. Calculated %: C 51.57; H 5.90; Se 30.82.

SUMMARY

1. Cyanoethylation of 2-acylselenophenes which do not have any alkyl radicals in 3-position proceeds quantitatively under the action of acrylonitrile in the presence of alcoholic alkali.

In this manner there were prepared for the first time the δ-oxo nitriles of the selenophene series: 1',1',1'-tris-(cyanoethyl)-2-acetoselenophene, 1',1'-bis-(cyanoethyl)-2-propioselenophene and 1'-methyl-1'-cyanoethyl-2-propioselenophene.

2. Cyanoethylation of 3-methyl-2-acylselenophenes failed to occur, apparently owing to steric hindrance, and only in the case of 3-methyl-2-acetoselenophene did the reaction take place but in a low yield, forming 3-methyl-1',1',1'-tris-(cyanoethyl)-2-acetoselenophene.

3. By alkaline hydrolysis of δ-oxo acids of this series: 1',1',1'-tris-(carboxyethyl)-2-acetoselenophene, 1',1'-bis-(carboxyethyl)-2-propioselenophene, 1'-methyl-1'-carboxyethyl-2-propioselenophene and 3-methyl-1',1',1'-tris-(carboxyethyl)-2-acetoselenophene.

4. Reduction of 1'-methyl-1'-cyanoethyl-2-propioselenophene with formic acid resulted in the formation of the previously undescribed 3,3-dimethyl-2-(2'-selenienyl)-6-piperidone.

5. It was shown, by the examples of preparation of 2-isobutyroselenophene, 3-methyl-2-isobutyroselenophene, 3,5-dimethyl-2-isobutyroselenophene and 3,4-dimethyl-2-isobutyroselenophene, that silicoanhydrides of saturated monobasic organic acids are convenient acylating agents for the selenophene nucleus and for preparation of ketones with branched radicals.

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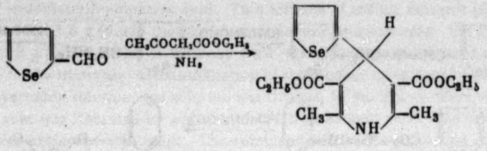
* Original Russian pagination. See C. B. Translation.

CHEMISTRY OF SELENOPHENE

XIV. REACTIONS OF SELENOPHENE-2-ALDEHYDE

Iu. K. Iur'ev and N. N. Mezentsova

It was shown in our previous papers [1-3] that selenophene-2-aldehyde possesses many reactions which are characteristic for aldehydes having an aromatic character. In the present work, continuing the study of reactions of selenophene-2-aldehyde, we subjected the latter to the Hantzsch reactionand obtained the diethyl ester of 2,6-dimethyl-4-(2'-selenienyl)-1,4-dihydropyridine-3,5-dicarboxylic acid by condensation with acetoacetic ester and ammonia.


Se
CHO
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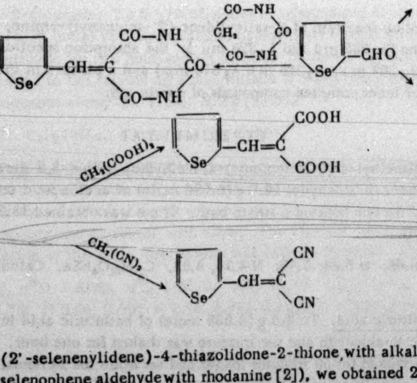
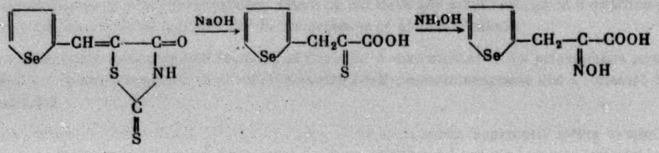
NH_3
Se
H
C_2H_5OOC
$COOC_2H_5$
CH_3
NH
CH_3

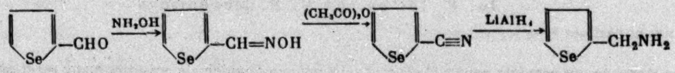
Condensation of selenophene-2-aldehyde with barbituric acid, with malonic acid and with malononitrile led, respectively, to 2-selenylidene-barbituric acid, 2-selenylidenemalonic acid and 2-selenylidenemalononitrile.


CO—NH
CH_2
CO
CO—NH
Se
CHO
Se
CH=C
CO—NH
CO
CO—NH
$CH_2(COOH)_2$
Se
CH=C
COOH
COOH
$CH_2(CN)_2$
Se
CH=C
CN
CN

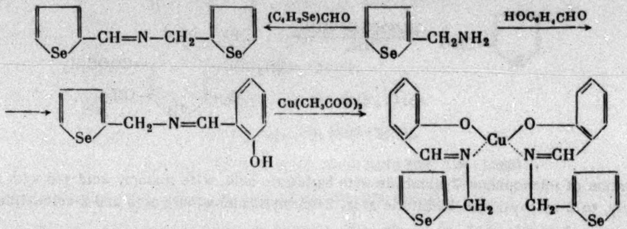
By decomposition of 5-(2'-selenenylidene)-4-thiazolidone-2-thione, with alkali (the ketone being the product of condensation of 2-selenophene aldehyde with rhodanine [2]), we obtained 2-thiono-3-(2'-selenienyl)-propionic acid in good yield, which was transformed into 2-oximino-3-(2'-selenienyl)-propionic acid by the action of hydroxylamine.



The oxime of selenophene-2-aldehyde served as the starting material for the preparation of 2-selenenylamine through the step of formation of 2-selenienylnitrile with its subsequent reduction with lithium aluminum hydride.



2-Selenenylamine readily entered a condensation with aldehydes – with selenophene-2-aldehyde and salicylaldehyde – forming N-(2′-selenenylidene)-2-selenenylamino and, respectively, N-salicylidene-(2′-selenenyl)-amine, while the latter yielded an inner complex compound of Cu^{++} under the action of copper acetate.



The ultraviolet absorption spectrum of N-salicylidene-(2′-selenenyl)-amine, taken in chloroform (Fig. 1) has two maxima of absorption (λ_1 255 mμ and λ_2 320 mμ); the absorption spectrum of the copper complex (Fig. 2) has three maxima (λ_1 257 mμ, λ_2 320 mμ λ_3 370 mμ) and a plateau in the region of 550 mμ-625 mμ, characteristic for this type of inner complex compounds of cupric ion.

EXPERIMENTAL

Diethyl ester of 2,6-dimethyl-4-(2′-selenienyl)-1,4-dihydropyridine-3,5-dicarboxylic acid. A mixture of 7 g (0.044 mole) of selenophene-2-aldehyde, 12.7 g (0.096 mole) of acetoacetic ester and 5.5 ml of 20% solution of ammonia was heated for one hour on a steam bath. There was obtained 10.9 g (65%) of the ester with m.p. 165-166° (from alcohol).

Found %: C 53.69, 53.66; H 5.84, 5.78; N 4.14, 4.08. $C_{17}H_{21}O_4NSe$. Calculated %: C 53.40; H 5.54; N 3.66.

2-Selenenylidenebarbituric acid. To 4.5 g (0.035 mole) of barbituric acid in 10 ml of water we added 5 g (0.031 mole) of selenophene-2-aldehyde and the mixture was shaken for one hour. Then, 80 g of sodium chloride was added, the mixture was shaken for 30 minutes longer and set aside for 24 hours. The precipitate was filtered off, washed with ice water and with ether. There was obtained 8 g (85%) of the acid with m.p. 309-310° (with decomposition).

Found %: C 39.97, 39.94; H 2.34, 2.46; N 10.17, 10.21. $C_9H_6O_3N_2Se$. Calculated %: C 40.15; H 2.23; N 10.37.

2-Selenenylidenemalonic acid. A solution of 6.5 g of selenophene-2-aldehyde (0.041 mole) and 9 g (0.086 mole) of malonic acid in 50 ml of anhydrous alcohol was saturated with dry ammonia, whereby a voluminous precipitate was formed. The mixture was heated for four hours on a water bath until the precipitate dissolved, was then cooled, poured into 100 ml of water and by addition to it of concentrated hydrochloric acid the above acid was separated from it; the acid had m.p. 229-230° (from water). Yield: 9 g (88.5%).

Found %: C 39.41, 39.44; H 2.38, 2.42. $C_8H_6O_4Se$. Calculated %: C 39.20; H 2.38.

2-Selenenylidenemalononitrile. To 11 g (0.07 mole) of selenophene-2-aldehyde in 15 ml of anhydrous alcohol there was added 5 g (0.075 mole) of malononitrile (m.p. 29°) and the mixture was heated at reflux on a water bath, treated with 3-4 drops of anhydrous pyridine and refluxed for 15-20 minutes longer. The resulting precipitate was separated and washed with alcohol; m.p. 91-92° (from alcohol). Yield: 11 g (78%).

Found %: C 46.43, 46.26; H 2.12, 2.10; N 13.77, 13.87. $C_8H_4N_2Se$. Calculated %: C 46.39; H 1.94; N 13.52.

2-Thiono-3-(2'-selenienyl)-propionic acid. A mixture of 13 g (0.047 mole) of 5-(2'-selenenylidene)-4-thiazolidone-4-thione (m.p. 234°) [2] and 55 ml of 15% solution of sodium hydroxide was heated for 30 minutes on a water bath and cooled; the resulting acid was isolated by addition of 10% hydrochloric acid; m.p. 118-120° (with decomposition). Yield: 10.9 g (94%).

Found %: 36.04, 36.11; H 2.73, 2.72. $C_7H_6O_2SSe$. Calculated %: C 36.07; H 2.59.

2-Oximino-3-(2'-selenienyl)-propionic acid. To a solution of sodium ethoxide (0.64 g of sodium in 18.5 ml of alcohol) we added 1.8 g (0.025 mole) of hydroxylamine hydrochloride; the solution was filtered, to the filtrate was added 2 g (0.009 mole) of 2-thiono-3-(2'-selenienyl)-propionic acid and the mixture was heated on a steam bath for 30 minutes. After distillation of the alcohol in vacuum, the residue was taken up in 5 ml of 5% sodium hydroxide solution, the solution was filtered, to the filtrate there was added 10 ml of ether and the resulting acid was liberated by addition of 10% hydrochloric acid. The ethereal layer was separated and the aqueous layer was extracted with ether. The combined ethereal extracts were dried over anhydrous sodium sulfate. After the distillation of ether, the residue was recrystallized from toluene; m.p. 139-140°. Yield: 1 g (50%).

Found %: C 36.55, 36.50; H 3.24, 3.16; N 5.55, 5.66. $C_7H_7O_3NSe$. Calculated %: C 36.22; H 3.04; N 6.03.

Oxime of selenophene-2-aldehyde. To 8 g (0.05 mole) of selenophene-2-aldehyde in 80 ml of alcohol we added a solution of 9.5 g (0.13 mole) of hydroxylamine hydrochloride and 8 g of potassium carbonate in 28 ml of water. The mixture was refluxed for one hour and set aside for 24 hours. After evaporation to one third of original volume, there was added to the residue an equal volume of water and the separated crystals were filtered off; m.p. 133-133.5° (from aqueous alcohol). Yield: 8.2 g (93.5%).

Found %: N 7.75, 7.81. C_5H_5ONSe. Calculated %: N 8.04.

2-Selenienylnitrile. To 8.8 g (0.05 mole) of oxime of selenophene-2-aldehyde we added 0.7 g of anhydrous sodium acetate and 9 ml of acetic anhydride. After initially violent boil-up, the mixture was refluxed for 40 minutes and after addition of 15 ml of water was refluxed for additional 2-3 minutes. It was then cooled, saturated with potassium carbonate and extracted with ether. The ethereal extract was dried over anhydrous sodium sulfate. After distillation of the ether, the residue was vacuum distilled. Yield: 6.9 g (88%).

B.p. 100-101° (12 mm), $n^{20}D$ 1.6120, d^{20}_4 1.6506, MR_D 32.66. $C_5H_3NSeF_2$. Calculated: 32.61. Found %: C 38.73, 38.76; H 2.25, 2.15; N 8.76, 8.90. C_5H_3NSe. Calculated %: C 38.48; H 1.93; N 8.97.

2-Selenenylamine. To an ethereal solution of lithium aluminum hydride (prepared from 21 g of aluminum bromide and 2.6 g of lithium hydride) we added a solution of 11.3 g (0.07 mole) of 2-selenienylnitrile in 100 ml of absolute ether. The mixture was heated for one hour on a water bath, after which there was added 100 ml of water and 200 ml of 20% solution of potassium tartrate. The ethereal layer was separated, the aqueous layer

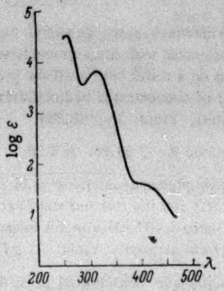


Fig. 1. Ultraviolet absorption spectrum of N-salicylidene-2'-selenenylamine in chloroform solution.

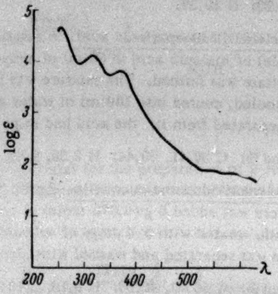


Fig. 2. Ultraviolet absorption spectrum of copper complex of N-salicylidene-2'-selenenylamine.

was extracted with ether and the combined ethereal extracts were dried over anhydrous sodium sulfate. After distillation of the ether, the residue was vacuum distilled. Yield: 7.6 g (66%).

B.p. 103-103.5° (15 mm), $n^{20}D$ 1.6044, d^{20}_4 1.5217. MR_D 35.49. $C_5H_7NSe F_2$. Calculated: 36.22. Found %: C 37.54, 37.55; H 4.47, 4.60; N 9.28, 9.12. C_5H_7NSe. Calculated %: C 37.54, H 4.40; N 8.75.

N-(2'-Selenenylidene)-2-selenenylamine. To 2.5 g (0.016 mole) of selenophene-2-aldehyde in 3 ml of methyl alcohol we added 2.56 g (0.016 mole) of 2-selenenylamine in 5 ml of methyl alcohol and the mixture was refluxed for two hours on a steam bath. There was obtained 4.3 g (91%) of light yellow crystals with m.p. 43-43.5° (from methyl alcohol).

Found %: C 39.99, 39.88; H 3.33, 3.22; N 4.69, 4.86. $C_{10}H_9NSe_2$. Calculated %: C 39.90; H 3.01; N 4.65.

N-Salicylidene-(2'-selenenyl)-amine. To 1.5 g (0.012 mole) of salicylaldehyde in 5 ml of alcohol we added 2 g (0.019 mole) of 2-selenenylamine; there was obtained 3.1 g (94%) of light yellow crystals with m.p. 52.5-53° (from alcohol).

Found %: C 54.48, 54.33; H 4.46, 4.50; N 5.27, 5.27. $C_{12}H_{11}ONSe$. Calculated %: C 54.55; H 4.19; N 5.31.

Copper complex of N-salicylidene-(2'-selenenyl)-amine. To 6 ml of a saturated solution of cupric acetate we added 2 ml of 1% alcoholic solution of N-salicylidene-(2'-selenenyl)-amine; there was obtained 0.046 g of crystals with dirty green color having m.p. 170-171°.

Found %: C 48.66, 48.59; H 3.68, 3.64. $C_{24}H_{20}O_2N_2CuSe_2$. Calculated %: C 48.87; H 3.40.

SUMMARY

1. Condensations of selenophene-2-aldehyde with acetoacetic ester and ammonia, with barbituric acid, with malonic acid and with malononitrile proceed normally and lead to the corresponding reaction products which contain the selenophene nucleus.

2. The reaction of hydroxylamine with 2-thiono-3-(2'-selenienyl)-propionic acid leads to formation of 2-oximino-3-(2'-selenienyl)-propionic acid.

3. The oxime of selenophene-2-aldehyde readily forms 2-selenophenenitrile, the reduction of which leads to 2-selenenylamine. The product of condensation of the latter with selenophene-2-aldehyde was N-(2'-selenenylidine)-2-selenenylamine; the product with salicylaldehyde was N-(2'-seleneylidine)-2-selenenyl-amine; the product with salicylaldehyde was N-salicylidene-(2'-selenenyl)amine, which forms an inner complex compound with cupric ion.

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CATALYTIC HYDROGENATION OF VINYLETHYLENE OXIDES

I. HYDROGENATION OF BUTADIENE OXIDE*

M. A. Aizikovich, I. A. Maretina and A. A. Petrov

In our previous studies we showed the dependence existing between the order of addition of various substances to organic α-oxides, their structures and the acid-base properties of the reagents or catalysts [1]. It was of interest to continue these studies in the direction of investigation of the order of addition of hydrogen to α-oxides.

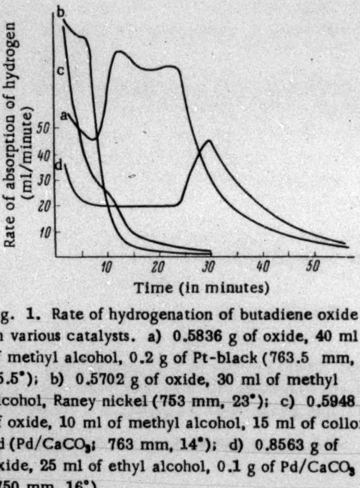

Fig. 1. Rate of hydrogenation of butadiene oxide on various catalysts. a) 0.5836 g of oxide, 40 ml of methyl alcohol, 0.2 g of Pt-black (763.5 mm, 15.5°); b) 0.5702 g of oxide, 30 ml of methyl alcohol, Raney nickel (753 mm, 23°); c) 0.5948 g of oxide, 10 ml of methyl alcohol, 15 ml of colloidal Pd ($Pd/CaCO_3$; 763 mm, 14°); d) 0.8563 g of oxide, 25 ml of ethyl alcohol, 0.1 g of $Pd/CaCO_3$ (750 mm, 16°).

The literature data on this problem are not numerous. To a greater or lesser degree the hydrogenation of α-oxides of ethylene, propylene, decylene, butadiene, methylcyclohexenes, as well as some aryl-substituted oxides and oxides containing other functional groups (carbonyl, carboxyl and others) have been studied [2-6].

One may conclude from the data on hydrogenation of oxides of olefins that the addition of hydrogen, at the moment of its liberation (in alkaline medium) or from the action of lithium aluminum hydride, occurs predominantly in accord with V. V. Markovnikov's rule. In the latter case, the relative yields of the two isomeric alcohols depend on the concentration of lithium aluminum hydride. Conversely, in the catalytic hydrogenation the addition of hydrogen to oxides proceeds predominantly contrary to the V. V. Markovnikov rule.

The greatest interest lies in the hydrogenation of α-oxides of the type of vinylethylene oxide, since one may expect in this case the formation of products of addition in 1,4-positions. The conjugation between the double and the oxide bonds has been observed more than once, as for example in the reactions with hydrogen halides [7] and organomagnesium compounds [1].

In the present paper there are described the results of experiments on catalytic hydrogenation of butadiene oxide over palladium, platinum and Raney nickel.

The majority of the experiments were run by us in methyl or ethyl alcohols with the use of palladium deposited on calcium carbonate as the catalyst. We were interested in the relative reactivity of the double bond and of the oxide ring, in the order of addition of hydrogen to the oxide ring, and finally, in the possibility of conjugation between the double bond and the oxide bond.

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*Studies in the field of chemistry of organic oxides. XV.

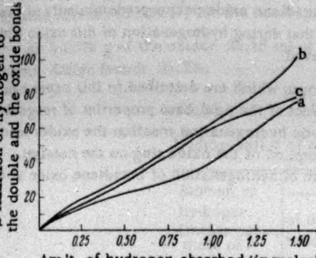


Fig. 2. Relative rate of hydrogenation of double (a) and oxide (b – experimental, c – calculated) bonds of butadiene oxide on $Pd/CaCO_3$.

The character of the curve of the rate of hydrogenation of butadiene oxide depends on the nature of the catalyst. The data which characterize this dependence are shown in Figure 1. With platinum black and palladium on calcium carbonate there occurs a sharp break (see the jump) in the hydrogenation rate. On the remaining catalysts the rate of hydrogenation drops uniformly. In hydrogenation with palladium on calcium carbonate the area of the constant rate of reaction increases with increasing amount of the catalyst. The appearance of a break in the curve of hydrogenation rate is evidently connected with the temporary partial poisoning of the catalyst.

The degree of hydrogenation of butadiene oxide also depends on the nature of the catalyst. In hydrogenation over platinum black in alcoholic medium there is absorbed 2.22 moles of hydrogen, while on Raney nickel the amount of absorbed hydrogen is 2.0 moles, and over palladium it is about 1.75 moles of hydrogen per one mole of the oxide.

Then, in the various stages of the hydrogenation process we determined the contents of unsaturated compounds in the reaction mixture (by the bromide-bromate method) as well as that of the oxides (Kerckow method [8]). The study was made over palladium on calcium carbonate by the technique of sample selection. The blank experiments for the control were set up by running the reaction to some definite stage. Data obtained by these two methods agreed comparatively well. The amount of hydrogen consumed in the hydrogenation of the oxide ring was also calculated by the difference between the amount of absorbed hydrogen and the amount of hydrogen utilized for hydrogenation of the double bonds. This calculation was necessary since the determination of unreacted oxides is not distinguished by high accuracy. It is evident from Figure 2 that until the addition of one mole of hydrogen the experimental and the calculated values on the determination of the oxide ring coincide with each other well. Later there are observed the ever increasing divergences; the oxide is consumed more rapidly than the rate of hydrogen addition. This clearly indicates the existence of side reactions. Such a process may be exemplified by the isomerization of the oxide into the corresponding aldehyde, especially enhanced at the final stages of the hydrogenation.

A comparison of the rate of hydrogenation curves for the oxide ring and for the double bond clearly shows that no strict selectivity exists in this case; however, the oxide ring is hydrogenated more rapidly than is the double bond.

We set up two experiments with larger samples of the oxide in order to study the final and the intermediate hydrogenation products of butadiene oxide: in the first experiment the hydrogenation was run to completion (1.75 moles of hydrogen added per mole of the oxide), while in the second experiment only one mole of hydrogen was added per mole of the oxide.

We obtained primary butyl alcohol from the complete hydrogenation of butadiene oxide. Some butyraldehyde was present in addition in the reaction mixture as determined by formation of the 2,4-dinitrophenylhydrazone. We failed to detect any secondary butyl alcohol by working with relatively small samples.

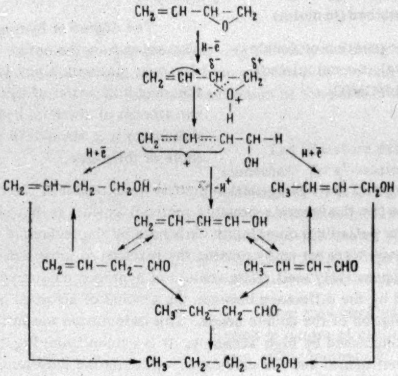
Thus we established that the oxide bond is predominantly cleaved at the secondary carbon atom.

Mainly crotyl alcohol, containing some alkyl carbinol and primary butyl alcohol, was obtained in the second experiment. The reaction mixture also contained an unsaturated aldehyde, evidently crotonaldehyde (as determined by formation of the 2,4-dinitrophenylhydrazone).

We determined the structures of the resulting alcohols by means of their physical constants and infrared spectra. One finds a considerable difference in the position of frequencies which correspond to the double bond in the infrared spectra of crotyl alcohol and allyl carbinol (Table 2). In the spectra of the hydrogenation products we found frequencies which corresponded to both alcohols, but the frequencies of crotyl alcohol were more prominent.

Thus, the addition of hydrogen during the hydrogenation of butadiene oxide occurs predominantly at the 1,4-positions of the oxide and the double bond. It should be noted that during hydrogenation of this oxide with lithium aluminum hydride the 1,4-addition of hydrogen is not observed.

The regularities in the reaction of butadiene oxide with hydrogen which are described in this paper can be connected most readily with the previously obtained data on the effect of the acid-base properties of reagents on the order of addition to oxides, if one supposes that in the catalytic hydrogenation reaction the oxides react in the form of oxonium compounds formed by the protons or by adsorption of the oxide ring on the catalyst. Thus, for example, starting with the first supposition, the mechanism of hydrogenation of butadiene oxide at the oxide ring may be shown in the following form:



The supposition that hydrogenation proceeds through an intermediate formation of aldehydes appears to be superfluous and improbable. It was shown, for example, that crotonaldehyde is hydrogenated much more slowly than butadiene oxide under the conditions used by us.

Thus, as the result of the present study it was established that vinylethylene oxide is hydrogenated by catalytically excited hydrogen first at the oxide bond with the addition of hydrogen at 1,4-and 1,2-positions and contrary to the V. V. Markovnikov rule. It has been shown by a new example – hydrogenation reaction – that the oxide bond is conjugated with the double bond in vinylethylene oxides.

EXPERIMENTAL

Butadiene oxide used in this work was prepared from the chlorohydrin [7]. The constants corresponded with the literature data. Colloidal palladium was prepared with the use of gum arabic as the protective colloid; one ml of the catalyst contained about 0.2 ml of palladium. Palladium on calcium carbonate was prepared by the usual method [11]; one g of the catalyst contained about 0.018 g of palladium.

The method of determination of the oxide bond was developed with pure propylene and butadiene oxides following the recipe for ethylene oxide [8, 9]. The method based on the binding of the oxide with hydrobromic acid gave unsatisfactory results. The best data for the determination of butadiene oxide by the Kerckow method were obtained through the use of a double excess of the absorbent solution with the reaction time of ten minutes. Increase of the reaction time led to lowered results.

Following are the results of two determinations of butadiene oxide.

1) 0.3132 g of the oxide; added 24.98 ml of absorbent solution. There was used 17.15 ml of sodium hydroxide solution (1.032 N) for the back-titration. Oxide found: 91.7%.

2) 0.3879 g of the oxide; 25.18 ml of absorbent solution. There was used 16.4 ml of sodium hydroxide solution. Oxide found: 91.2%.

TABLE 1

Hydrogenation of Butadiene Oxide

Amount of hydrogen (moles per mole of oxide)	Amount reacted (moles)		
	of the double bond	of the oxide ring	
		experimental data	calculated
0.25	11.0	17.8	14.0
0.50	20.8, 22.2	29.2	29.2, 27.8
0.75	28.6	47.0	46.4
1.00	40.5, 39.6	62.1	59.5, 60.4
1.25	58.3	78.0	66.7
1.50	75.1	100.0	74.9

Note: Separate samples were hydrogenated: 0.01 mole of oxide, 0.2 g palladium on calcium carbonate, 25 ml of ethyl alcohol.

For obtaining more accurate data during the hydrogenation of butadiene oxide we set up some blank experiments with a mixture of the oxide, the alcohol and the catalyst. On the basis of these results a small correction was applied for the calculation of the amount of unreacted oxide.

The determination of the double bond in butadiene oxide by the bromide-bromate method gave good results: In several samples there was found some 98% of the oxide.

The hydrogenation was run in the usual boat with a valve in the S. V. Lebedev apparatus.* The oxide was charged inside thin-walled glass ampules to avoid losses.

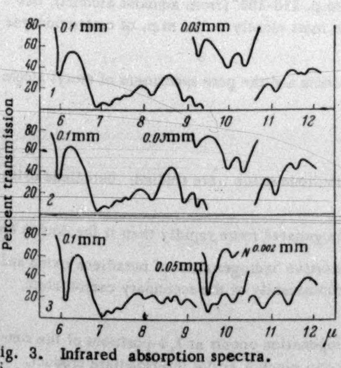


Fig. 3. Infrared absorption spectra.
1) Mixture of hydrogenation products, 2) crotyl alcohol, 3) allylcarbinol.

The conditions of the experiments on exhaustive hydrogenation of the oxide are shown in the corresponding figure.

The results of some experiments in the study of the relative rate of hydrogenation of the double bond and of the oxide ring are shown in Table 1.

In the exhaustive hydrogenation of 6.63 g of butadiene oxide in 95 ml of ethyl alcohol in the presence of 1.91 g of palladium on calcium carbonate there was absorbed 3722 ml of hydrogen (765 mm, 15°) which corresponds to about 1.7 moles per mole of the oxide. Primary butyl alcohol, evidently with a small admixture of the crotyl alcohol, was obtained by distillation of the mixture through a Widmer column: b. p. 117-119°, d^{20}_4 0.8201, $n^{20}D$ 1.4005, which was close to the literature data [10].

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* The authors express their gratitude to A. I. Lebedeva for the apparatus for hydrogenation and for valuable advice.

Butyraldehyde was found in the alcoholic solution. It was isolated as 2,4-dinitrophenylhydrazone with m.p. 126° (from alcohol) [10].

Found %: N 22.36, 22.54. $C_{10}H_{12}O_4N_4$. Calculated %: N 22.21.

From hydrogenation of 8.1 g of butadiene oxide in methyl alcohol over palladium-on-calcium carbonate catalyst (this catalyst was added in two portions) in which 2728 ml of hydrogen had been absorbed (755 mm, 15°), which amount corresponded to 1:1 molar ratio of the oxide and hydrogen, we obtained 4.4 g of mixed alcohols with b.p. 116-122°, d^{20}_4 0.8480, n^{20}_D 1.4205, after distillation through a 25 cm Widmer column. We found 75% unsaturated alcohols in this mixture by the bromide-bromate method. This mixture was closer to crotyl alcohol in its physical constants. The residue after the distillation of these alcohols amounted to but one gram and had the characteristics of a polymer.

TABLE 2

Infrared Transmission Spectra (in μ)

Hydrogenation products (alcohol mixture)	Crotyl alcohol	Allylcarbinol	Remarks
5.98 c	5.98	—	$\nu_{C=C}$
6.09 cp	—	6.09 c	
6.89 o. c	6.89 o. c	6.92 o. c	
7.20 * cp	7.20 cp	7.26 сл	
7.47 * cp	7.50 * cp	7.43 сл	
7.63 * cp	7.64 * cp	—	
8.19 c	8.19 c	7.94 сл	
—	—	8.39 cp	
—	—	8.50 cp	
8.97 c	8.98 c	8.88 cp	
9.27 c	9.26 c	9.51 o. c	ν_{C-O}
—	—	9.77 сл	
9.97 o. c	9.97 o. c	10.08 c	
—	—	10.28 cp	γ'_{CH} in $CH_2=CH-$
10.34 o. c	10.34 o. c	—	γ'_{CH} in $-CH=CH-$
—	—	10.81 c	γ'_{CH} in $CH_2=CH-$
11.11 c	11.11 c	—	
11.57 cp	11.57 cp	11.48 cp	

Note: c, strong; cp, medium; o.c, very strong; сл , weak.

An aldehyde, which formed a p-nitrophenylhydrazone with m.p. 175-180° (from aqueous alcohol), was found in the alcoholic part of the distillate; this derivative came most closely to the m.p. of crotonaldehyde p-nitrophenylhydrazone (184°) [10].

The data on the infrared spectra of the hydrogenation products and the pure specimens of crotyl alcohol and allyl carbinol are given in Table 2 and Figure 3.

SUMMARY

1. The rate and the order of catalytic hydrogenation of butadiene oxide were studied; butadiene oxide used was 1,2-epoxy-3-butene.

2. It was shown that the oxide ring of this substance is hydrogenated more rapidly than is the double bond.

3. Some primary butyl alcohol was obtained from the exhaustive hydrogenation of butadiene oxide and it was thus established that the opening of the oxide ring occurs predominantly at the secondary carbon atom, contrary to the V. V. Markovnikov rule.

4. It was shown that the hydrogen addition during the hydrogenation occurs at 1,4-positions of the conjugated $C=C-\underbrace{C-O-C}$ system, with resulting formation of crotyl alcohol as the intermediate product.

5. A supposition was made about the intermediate formation of oxonium compounds during the catalytic hydrogenation of oxides, as the result of which phenomenon one observes the addition of hydrogen a direction that is contrary to the V. V. Markovnikov rule.

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CATALYTIC HYDROGENATION OF VINYLETHYLENE OXIDES

II. HYDROGENATION OF CHLOROPRENE OXIDE*

M. A. Aizikovich and A. A. Petrov

It was shown in the preceding paper that during catalytic hydrogenation of butadiene oxide there occurs the addition of hydrogen at both the oxide and the double bonds, with the first process having the somewhat greater rate [1]. The primary hydrogenation product is predominantly crotyl alcohol (1,4-addition). It was interesting to compare this result with the data on catalytic hydrogenation of oxides containing electronegative substituents at the double bond, the reaction being run under the same conditions. In the present paper are described the results of some experiments on hydrogenation of chloroprene oxide (1,2-epoxy-3-chloro-3-butene) over palladium and nickel.

In the study of the process of hydrogenation of chloroprene oxide we were interested, as before, in the relative reactivity of the oxide and the double bonds as well as that of the halogen, and in the order of the addition of hydrogen to the oxide ring.

The character of the curves of the rate of hydrogenation differs somewhat in this case from that found earlier for butadiene oxide and depends also on the nature of the catalyst. The data are shown in Figure 1.

The curves of the rate of hydrogenation of chloroprene oxide on colloidal palladium and on palladium-on-calcium carbonate have the same form. On Raney nickel one observes a more rapid fall of the rate of hydrogenation after the addition of one mole of hydrogen. Over colloidal palladium there is absorbed in all 2.7-2.8 moles of hydrogen per mole of the oxide, while over palladium on calcium carbonate one observes the complete hydrogenation. In the last case, the sharp drop of the hydrogenation rate occurs considerably later than in the case of butadiene oxide, specifically after absorption of over 90% of hydrogen. The greater completeness of hydrogenation of chloroprene oxide is caused by its lesser tendency to polymerization, alcoholysis and isomerization under the conditions of hydrogenation.

Chloroprene oxide is hydrogenated considerably more slowly in comparison with butadiene oxide. In hydrogenation over colloidal palladium, the addition of a large excess of sodium acetate leads to a considerable increase of the rate of hydrogenation. Evidently, under these conditions one eliminates the poisoning of the catalyst by hydrochloric acid formed during the hydrogenation. In hydrogenation over palladium on calcium carbonate, the hydrochloric acid is bound by the catalyst support. In working with small samples of the oxide, the evolving carbon dioxide dissolves in the alcohol and does not interfere with the hydrogenation. This was established for the first time in our laboratory for this specific case.

We met in the case of chloroprene oxide a number of considerable difficulties in studying the relative reactivity of the oxide and the double bonds. Here, both the determination of the oxide bond and the determination of unsaturation gave poor results. We judged the amount of double bonds entering the reaction by the amount of chloride ion formed. It was shown by special experiments that, after the destruction of the oxide at the various stages of the process of hydrogenation, further hydrogenation proceeds in such a manner that the amount of the resulting chloride ion corresponds exactly, in equivalents, to half the amount of hydrogen, in moles, that is consumed in the hydrogenation. These data can be explained starting from the supposition that chlorine is replaced immediately after the addition of hydrogen to the double bond.

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* Studies in the field of chemistry of organic oxides. XVI.

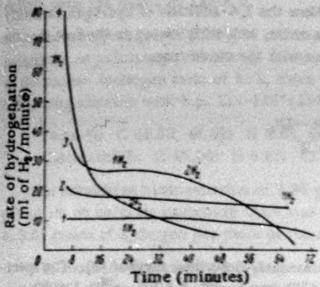


Fig. 1. Summary rate of hydrogenation of chloroprene oxide over various catalysts. 1) 0.9762 g of the oxide, 55 ml of methyl alcohol, 0.99 g of Pd/CaCO$_3$ (777.8 mm, 18°); 2) 1.0072 g of the oxide, 35 ml of ethyl alcohol, 20 ml of colloidal palladium (771 mm, 18°); 3) 1.1618 g of the oxide, 25 ml of methyl alcohol, 3.6 g of sodium acetate, 15 ml of colloidal palladium (764 mm, 26°); 4) 0.9907 g of the oxide, 50 ml of ethyl alcohol, 3.6 g of sodium acetate, about 3 g of Raney nickel (759.5 mm, 19.5°).

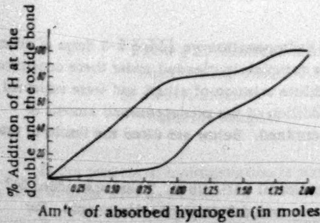


Fig. 2. The rate of hydrogenation of oxide (a) and double (b) bonds in chloroprene oxide.

We judged the amount of hydrogen consumed for the hydrogenation of the oxide ring by the difference between the amount of absorbed hydrogen and the amount of hydrogen used for hydrogenation of the double bond and substitution of chlorine atoms.

The resulting data are shown in Figure 2. These show that in the case of chloprene oxide there takes place at the beginning of the process a predominant hydrogenation of the oxide ring. In absorption of one mole of hydrogen per one mole of the oxide, the oxide ring enters the reaction by some 76.5%. Thus, chloroprene oxide is hydrogenated much more selectively than is butadiene oxide evidently owing to the lesser reactivity of the double bond, substituted by a halogen, in respect to the catalytically excited hydrogen.

We set up some experiments with larger samples of chloroprene oxide for determination of the structure of hydrogenation products.

We obtained normal butyl alcohol by exhaustive hydrogenation. In the experiment with the 1:1 ratio of oxide: hydrogen we obtained an unsaturated chlorine-containing alcohol, as the principal product. As the result of hydrogenation of chloroprene oxide one may expect the formation of three unsaturated chlorine-containing alcohols (I-III).

$$\underset{(I)}{CH_2{=}CCl{-}CH_2{-}CH_2OH} \qquad \underset{(II)}{CH_3{-}CCl{=}CH{-}CH_2OH}$$

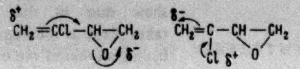
$$\underset{(III)}{CH_2{=}CCl{-}CHOH{-}CH_3}$$

The formation of alcohol (III) in any significant amounts was excluded since in the exhaustive hydrogenation of chloroprene oxide there was obtained only primary butyl alcohol. β-Chlorocrotyl alcohol (II) has been described in the literature [2]. In its physical constants the product of hydrogenation of chloroprene oxide differed somewhat from this alcohol.

The composition of the mixture of the alcohols obtained by us in the hydrogenation was established on the basis of their infrared spectra along with the infrared spectrum of chlorocrotyl alcohol (II). The latter, like crotyl alcohol, has a frequency of the double bond at about 1670 cm^{-1}, while allylcarbinol absorbs at 1640 cm^{-1}. Evidently chloroallylcarbinol (I) should absorb in the same region since it has a singly substituted double bond.

In the infrared spectrum of the products of hydrogenation of chloroprene oxide there were two frequencies of the double bond at 1669 and 1639 cm^{-1} with a small difference in intensities. The first frequency undoubtedly belonged to chlorocrotyl alcohol (II), while the second one evidently was that of chloroallylcarbinol (I). Thus, it was established that in hydrogenation of chloroprene oxide the addition of hydrogen occurs at both the oxide ring as well as in the 1,4-position, i. e., there occur the simple and the conjugated addition of hydrogen.

The formation of any significant amount of aldehydes was not observed in hydrogenation of chloroprene oxide. Consequently, the experiments on hydrogenation of chloroprene oxide could not be interpreted starting with the supposition of an intermediate formation of aldehydes [1]. Here the 1,4-addition of hydrogen evidently takes place, however, to a lesser degree than in the case of butadiene oxide, evidently owing to the fact that the chlorine atom takes the double bond to some extent out of conjugation with the oxide ring.



EXPERIMENTAL

Chloroprene oxide was obtained from the bromohydrin by the previously described method [3]. The specimen with the following constants was used for this work: b.p. 61-62° (150 mm), d^{20}_4 1.1652, $n^{20}D$ 1.4599.

The conditions of hydrogenation and the methods of preparation of the catalysts were the same as in the previous work* [1]. The chloride ion was determined by titration with mercuric nitrate or sodium hydroxide. The amount of hydrogen utilized for hydrogenation of the double bonds was determined by the amount of the chloride ion. The following experiments served as the basis for such a determination.

TABLE 1

Expt. No.	Catalyst	Relative amount of catalyst	Am't of H_2 absorbed (moles)	Am't of chloride ion (%)	Remarks
1	Colloidal palladium	1	2.70	95.66	Added sodium acetate · CH_3COONa
2	"	1.5	2.72	95.11	
3	"	2.0	2.82	—	—
4	"	2.5	2.75	—	—
5	$Pd/CaCO_3$	—	3.00	99.27	—
6	Raney nickel	—	2.80	—	—

To several samples of the reaction mixture at various stages of hydrogenation we added 2-3 drops of sulfuric acid and the mixtures were set aside for 2 weeks. The oxide ring was completely cleaved under these conditions. Then the mixtures under examination were precisely neutralized by dilute solution of alkali and were subjected to hydrogenation in the presence of colloidal palladium. After the addition of the predetermined amount of hydrogen, the amount of free hydrogen chloride in the liquid was determined. Below are cited the results of two determinations from one experiment.

1. 4.188 g of chloroprene oxide, 192 ml of alcohol, 60 ml of colloidal palladium. There was added 242 ml of hydrogen (758.5 mm, 24°). A sample of 10 ml was taken. There was added 3 drops of sulfuric acid. For hydrogenation of the mixture 64.4 ml (0.0027 mole) of hydrogen (755 mm, 18°) was utilized. In the liquid there was found 0.0014 mole of hydrogen chloride.

2. In the same experiment of hydrogenation there was taken a sample after the addition of 1.55 moles of hydrogen per one mole of the oxide. There was added 35 ml (0.0015 mole) of hydrogen (761.6 mm, 14°). There was found 0.0007 mole of hydrogen chloride.

The results of the experiments on the determination of the degree of hydrogenation are shown in Table 1 and Figure 1. In all experiments the amount of the oxide was of the order of 1 g, the solvent was methyl or ethyl alcohol (35-60 ml), the amount of colloidal palladium varied from 10 to 25 ml, that of palladium on calcium carbonate was 1 g (0.025 g of Pd), and that of Raney nickel was about 3 g.

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* Chloroprene oxide and the solutions for hydrogenation were introduced into the boat by creation of slight vacuum in the latter.

The results of the experiments on the study of the relative rate of hydrogenation of the oxide ring and the double bond are shown in Table 2.

In hydrogenation of 5.12 g of chloroprene oxide in 30 ml of methyl alcohol in the presence of 1.14 g of palladium on calcium carbonate up to the uptake of 1176 ml of hydrogen (761.8 mm, 19°) which corresponded to the oxide: hydrogen ratio of 1 : 1, there was obtained 2.7 g (52% based on hydrogen) of unsaturated chlorine-containing alcohols with b.p. 114-116° (150 mm), d^{20}_4 1.1110, $n^{20}D$ 1.4640.

Found %: C 45.53, 45.62; H 6.67, 6.68; Cl 32.80; number of active hydrogens 1.07. C_4H_7OCl.
Calculated %: C 45.06; H 6.62; Cl 33.29; active H 1.0.

In exhaustive hydrogenation of 7.95 g of the oxide in 44 ml of methyl alcohol in the presence of 6 g of palladium on calcium carbonate there was taken up 4710 ml of hydrogen (753.8 mm, 18.3°) which corresponded to 2.57 moles of hydrogen per mole of the oxide.

In another experiment on hydrogenation of 8.11 g of the oxide in 45 ml of methyl alcohol in the presence of 7.5 g of palladium on calcium carbonate there was absorbed 4746 ml of hydrogen (750.2 mm, 24.5°) which corresponded to 2.47 moles of hydrogen per mole of the oxide.

TABLE 2

Colloidal palladium (40 ml)*			Palladium on calcium carbonate (0.3-1 g)**		
am't of H_2 absorbed (moles)	reacted (in mole %)		am't of absorbed H_2 (moles)	reacted (in mole %)	
	chlorine (double bond)	oxide ring		chlorine (double bond)	oxide ring
0.25	2.20	20.60	0.26	2.83	20.34
0.50	4.62	40.76	0.51	6.01	38.98
1.00	12.75	74.50	1.00	11.74	76.52
1.44	34.81	74.38	1.51	35.25	80.50
1.90	57.56	74.88	1.92	54.40	83.20
2.72 ***	95.11	82.00	2.51	76.50	98.00
			3.00	99.27	100.00

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* 2.339 g of chloroprene oxide, 117 ml of CH_3OH; samples of 25 ml taken.

** Separate samples of 0.5-1 g of the oxide were hydrogenated in 40-50 ml of methyl alcohol.

*** Separate sample.

In the process of hydrogenation it was necessary to stop the experiments and to blow the system free of carbon dioxide with hydrogen.

By distillation of the alcoholic solution of the hydrogenation products obtained in these two experiments there was isolated 4 g of primary butyl alcohol (yield of 42% based on hydrogen) with b.p. 116-118°, d^{20}_4 0.8185, $n^{20}D$ 1.3989, which agreed with the literature data [4].

In these and other experiments tests were made for the content of aldehydes in the alcoholic solution. The aldehydes were not found (test with 2,4-dinitrophenylhydrazine) in amounts any greater than traces.

SUMMARY

1. The rate and the order of addition of catalytically excited hydrogen to chloroprene oxide were studied.

2. It was shown that chloroprene oxide is hydrogenated much more slowly than butadiene oxide and the process is selective: the oxide ring adds hydrogen with greater speed than does the double bond.

3. In partial hydrogenation of chloroprene oxide there was formed a mixture of two chlorobutenyl alcohols, while in complete hydrogenation normal butyl alcohol was formed. Formation of aldehydes was not observed.

4. It was established that the oxide ring is opened at the side of the secondary carbon atom, while addition of hydrogen at 1,4-positions occurs to a considerable degree owing to the conjugation of the oxide and the double bonds.

5. It was shown that catalytic hydrogenation over palladium on calcium carbonate may serve as a method for quantitative determination of halogen in halogen substituted oxides.

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* Original Russian pagination. See C. B. Translation.

** In Russian.

ON THE REACTION OF DIALKYL HYDROGEN PHOSPHITES WITH ALDEHYDES AND KETONES

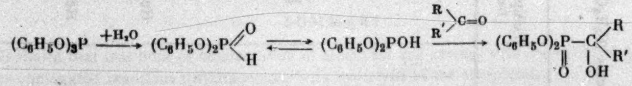
XVIII. PHENYL ESTERS OF α-HYDROXYALKYLPHOSPHONIC ACIDS

V. S. Abramov and N. A. Semenova

The synthesis of phenyl esters of various α-hydroxyalkylphosphonic acids by condensation of acid esters of phosphorous acid with aldehydes and ketones, developed by us [1], meets some difficulties in the preparation of diphenyl hydrogen phosphite. However it turned out to be possible to accomplish these syntheses by another route.

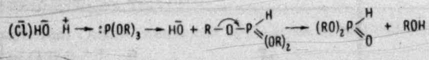
A. E. Arbuzov [2] showed that the action of acidified water on complete esters of phosphorous acid leads to the formation of the acidic esters. In developing this work A. E. Arbuzov and M. G. Imaev [3] studied the hydrolysis and transesterification of esters of phosphorous acid and found some general rules. Specifically, in hydrolysis of phosphites, the rate of hydrolysis changes in solutions of various substances. Acetone retards the hydrolysis and yields esters of α-hydroxyisopropylphosphonic acid.

The ease of preparation of the phenyl ester of phosphorous acid and its availability make it possible to use the hydrolysis reaction for the synthesis of diphenyl hydrogen phosphite, while if the reaction of hydrolysis is run in the presence of compounds containing a carbonyl group, one can synthesize the phenyl esters of α-hydroxyalkylphosphonic acids. The reaction of formation of diphenyl hydrogen phosphite in this case would proceed consecutively with the reaction of condensation with the carbonyl compounds.



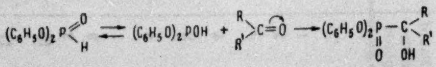
$$(C_6H_5O)_3P \xrightarrow{+H_2O} (C_6H_5O)_2P{<}^{O}_{H} \rightleftarrows (C_6H_5O)_2POH \xrightarrow{{}^{R}_{R'}{>}C=O} (C_6H_5O)_2\underset{\overset{\|}{O}}{P}-\underset{\overset{|}{OH}}{C}{<}^{R}_{R'}$$

The process of hydrolysis with acidified water, as indicated by A. E. Arbuzov [2], proceeds vigorously with evolution of much heat and, as one should surmise, has a chain character, proceeding by the following scheme:



$$(\bar{Cl})H\bar{O}\ \overset{+}{H} \rightarrow :P(OR)_3 \rightarrow H\bar{O} + R-\bar{O}-P{<}^{H}_{(OR)_2} \rightarrow (RO)_2P{<}^{H}_{O} + ROH$$

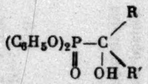
The resulting diphenyl hydrogen phosphite reacts in tautomeric form, in a condensation reaction, with aldehydes and ketones, in the presence of which the condensation and hydrolysis are being run:



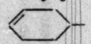
$$(C_6H_5O)_2P{<}^{O}_{H} \rightleftarrows (C_6H_5O)_2POH + {}^{R}_{R'}{>}C=O \rightarrow (C_6H_5O)_2\underset{\overset{\|}{O}}{P}-\underset{\overset{|}{OH}}{C}{<}^{R}_{R'}$$

The course of the condensation reaction becomes possible since the tautomeric equilibrium is shifted toward the trivalent form owing to the properties of the phenyl radical. The consecutively running reactions

Phenyl Esters of α-Hydroxyalkylphosphonic Acids



$(C_6H_5O)_2P(=O)-C(OH)(R)(R')$

No. of compound	R	R′	Temperature rise (from – to)	Solvent for recrystallization	Melting point	Yield (in %)	Phosphorus content (%)	
							found	calculated
1	CH_3CH_2	H	24–57°	Aqueous alcohol	87–87.5°	20	10.51, 10.61	10.61
2	$CH_3CH_2CH_2$	H	22–50	Cyclohexane	63–64	32	10.20, 10.13	10.13
3	CCl_3	H	22–60	Cyclohexane + alcohol (10 : 1)	131–131.5	80	8.03, 8.12	8.12
4	C_6H_5	H	25–52	96% Alcohol	147–148	24	9.26, 9.12	9.12
5		H	None	Aqueous alcohol Cyclohexane	112–114	88	8.89, 9.03	9.01
6	$O_2NC_6H_4$-m	H	25–52	Aqueous alcohol Cyclohexane	98.5–100	20	8.06, 8.09	7.99
7	CH_3	CH_3	25–56	Cyclohexane	116–117	32	10.80, 10.73	10.62
8	CH_2Cl	CH_3	23–61	Aqueous alcohol	122–123	22	9.32, 9.26	9.49
9	CH_2Cl	CH_2Cl	23–50	Aqueous alcohol	112–114	18	8.62, 8.55	8.58
10	C_6H_5	CH_3	Heating	Cyclohexane-alcohol (15 : 1)	126–127.5	20	8.73, 8.82	8.76
11	$-CH_2-CH_2-CH_2-CH_2-$		22–45°	Cyclohexane	126–127	25	9.64, 9.58	9.74
12	$-CH_2-CH_2-CH_2-CH_2-CH_2-$		Heating	Cyclohexane	127–128	30	9.23, 9.40	9.34

of hydrolysis and condensation were usually accompanied by heat evolution with some rare exceptions. The resulting phenyl esters of α-hydroxyalkylphosphonic acids were isolated in most cases in the crystalline state after the removal of phenol formed during the hydrolysis reaction. The esters of α-hydroxyalkylphosphonic acids were purified by recrystallization from suitable solvents.

The reaction of hydrolysis of ethyl ester of phosphorous acid in the presence of benzaldehyde and cyclohexanone, under conditions analogous to those used for the phenyl ester, failed to give esters of α-hydroxyalkylphosphonic acids. In this case the esters of α-hydroxyalkylphosphonic acids are formed either on addition of sodium alcoholate to the reaction mixture when the reaction proceeds rapidly with evolution of much heat and its subsequent transformation into a solidly crystalline mass, or after a very prolonged standing a period of months. The different course of these reactions may evidently be explained by the state of the tautomeric equilibrium of the two forms.

The phenyl esters of various α-hydroxyalkylphosphonic acids synthesized by us are shown in the table.

EXPERIMENTAL

The reaction of hydrolysis of triphenyl phosphite with the subsequent condensation of the resulting diphenyl hydrogen phosphite with carbonyl compounds was run in the following manner. Into a small flask there was placed equimolar amounts of triphenyl phosphite and the aldehyde or ketone. The components of the reaction were stirred. Then there was added the calculated (equimolar) amount of water and the whole was again shaken thoroughly. Usually the temperature of the reaction mixture rose by 30-35° and only in some cases was heating required, as for example in the reaction with acetophenone. Then the reaction mixtures were kept at room temperature or were heated on a water bath to complete the reaction. The reaction mixture was treated with water to remove the phenol formed in the hydrolysis reaction, after which crystallization of the substance usually occurred.

The substances obtained after recrystallization were, in most cases, well formed crystals. We failed to find a suitable solvent for the phenyl ester of α-hydroxy-β,β-dichloroisopropylphosphonic acid. Low yields of the esters are explained by large losses during the removal of phenol and in recrystallization.

We ran many more reactions than are shown in the table. The remaining products failed to crystallize after a long period of time and remained as viscous oily liquids, the isolation and purification of which to the chemically pure state was difficult.

SUMMARY

1. It was shown that reactions of condensation of aldehydes and ketones with dialkyl hydrogen phosphites may proceed as conjugated reactions simultaneously with hydrolysis of the phosphites.

2. There were prepared some phenyl esters of various α-hydroxyalkylphosphonic acids.

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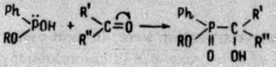
**In Russian.

ON THE REACTION OF ARYL(ALKYL)PHOSPHINIC ACIDS WITH ALDEHYDES AND KETONES

XIX. ESTERS OF α-HYDROXYALKYLPHENYLPHOSPHINIC ACIDS

V. S. Abramov and M. I. Kashirskii

It was shown previously that dialkyl hydrogen phosphites add readily to the C=O bond of the carbonyl group of aldehydes and ketones and yield esters of α-hydroxyalkylphosphonic acids [1]. It was of interest to extend these studies as well to the acid esters of aryl- or alkylphosphinic acids and one could suppose that these would also react readily with carbonyl compounds, just like dialkyl hydrogen phosphites. The condensation of acid esters of aryl(alkyl)phosphinic acids with aldehydes and ketones should lead to esters of α-hydroxyalkylaryl (alkyl)phosphinic acids. The reaction may be represented by the following scheme:



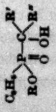
We studied the reaction of acid esters of phenylphosphinic acid with aldehydes and ketones and found that these reactions proceed with formation of esters of α-hydroxyalkylphenylphosphinic acids. The reactions of acid esters of phenylphosphinic acid with aldehydes proceed with slight heat evolution, while the reactions with ketones occur with a slight drop of the temperature. In the latter case a solution of the ketone with absorption of heat evidently occurs. The phenomenon of a drop in temperature in dissolution of various substances in dialkyl hydrogen phosphites was observed by us on many occasions. Introduction of substances with basic character (as catalysts) into the reaction mixture, such substances as sodium alcoholate in alcohol, affects the course of the reaction but little. Therefore, the reaction of acid esters of phenylphosphinic acid with aldehydes and ketones were run without a catalyst after prolonged standing of the reaction mixture at room temperature or by heating on a water bath. The factor indicating the progress of the reaction was the appearance and the growth of crystals of the resulting ester of α-hydroxyalkylphenylphosphinic acids. The reaction was considered complete when the entire reaction mixture either changed to crystalline form or the crystal growth stopped. Esters of α-hydroxyalkylphenylphosphinic acids were purified by recrystallization from a suitable solvent. Their constants are shown in the table.

After completion of our work we became aware of the paper by R. Miller and co-workers about the addition of dialkylphosphinous acids to aldehydes and ketones [2]. The addition reactions were run by them in anhydrous alcohol by the action of sodium alcoholate on the reaction mixture.

These authors prepared oxides of α-hydroxyalkyldialkylphosphines, or as these were named by them – disubstituted phosphenyl alcohols – for the first time. We also ran some work in this direction. Thus far we have not succeeded in obtaining positive results owing to the difficulties met in the isolation of diethylphosphinous and other dialkylphosphinous acids.

The reaction of addition to the carbonyl group of aldehydes and ketones proceeds successfully with both the dialkyl hydrogen phosphites and with phenyl(alkyl)phosphinic and dialkyl(aryl)phosphinous acids and has a general character.

Esters of α-Hydroxyalkylphenylphosphinic Acid



$C_6H_5(RO)P(=O)-C(OH)R'R''$

No. of compound	R	R'	R"	Temperature rise (from–to)	Solvent for recrystallization	Melting point	Yield (in %)	% P found	% P calculated
1	CH_3	CCl_3	H	18—41°	Acetone + water	122—123°	23	10.31, 10.41	10.21
2	CH_3	m-$O_2NC_6H_4$	H	18—32	Anhydrous alcohol	155—156	20	9.86, 10.03	10.09
3	C_2H_5	C_3H_7	H	17—28	"	122—123.5	15	12.46	12.80
4	C_2H_5	C_6H_5	H	17—34	96% Alcohol	182—182.5	25	11.12, 11.18	11.23
5	C_2H_5	m-$O_2NC_6H_4$	H	17—22	Acetone	120—121	20	9.34, 9.48	9.65
6	C_4H_9	C_6H_5	H	18—25	Acetone + water	76— 78	25	10.03, 10.26	10.20
7	C_4H_9	m-$O_2NC_6H_4$	H	18—20	Anhydrous alcohol	120—121.5	23	8.68, 8.70	8.90
8	iso-C_4H_9-	C_6H_5	H	18—22	"	100—101	58	9.95, 10.08	10.19
9	iso-C_4H_9-	m-$O_2NC_6H_4$	H	18—28	"	142—143	66	8.75, 8.84	8.88
10	iso-C_4H_9-	CH_3	CH_3	18—15	Acetone	94— 95.5	16	11.97, 12.00	12.10
11	iso-C_4H_9-	C_6H_5	CH_3	18—16	96% Alcohol	150—151	28	9.67, 9.81	9.74

EXPERIMENTAL

The reactions of acid esters of phenylphosphinic acid with aldehydes and ketones were run as follows. Into a small flask or ampule there was placed 0.02-0.05 mole of the acid ester of phenylphosphinic acid and to this was added an equimolar amount (0.02-0.05 mole) of the aldehyde or ketone. In mixing of the acid ester with aldehydes a rise of temperature of 4° to 17° was usually observed, while in mixing with ketones there occurred a drop of temperature by 2-3°. The reaction mixture was either allowed to stand at room temperature or was heated on a water bath. The reactions with aldehydes were usually run at room temperature. In this case the formation of esters of α-hydroxyalkylphenylphosphinic acids was observed after 3-7 days. The reactions with ketones were run by heating on a water bath and were completed in 36-48 hours. The esters of α-hydroxyalkylphenylphosphinic acids crystallized either directly in the reaction vessel or after their introduction into a suitable solvent. The esters were recrystallized from alcohol, aqueous alcohol, acetone, cyclohexane or their mixtures. The yields of crude products were good and amounted to 70-90%. However, large losses occurred during the purification and the yield of pure products was lowered considerably. It is possible that a partial cleavage of the condensation product into the starting materials takes place during the recrystallization. Esters of α-hydroxyalkylphenylphosphinic acids were colorless crystalline substances.

SUMMARY

1. It was shown that acid esters of phenylphosphinic acid react with aldehydes and ketones and form esters of α-hydroxyalkylphenylphosphinic acids. The condensation reactions proceed without a catalyst, those with aldehydes occur with evolution of heat.

2. There were prepared eleven esters of various α-hydroxyalkylphenylphosphinic acids.

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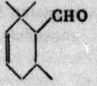
DIENE CONDENSATIONS OF GEM-SUBSTITUTED BUTADIENES. I.

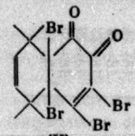
I. N. Nazarov and M. V. Mavrov

It was noted by a number of workers that cis-1-substituted dienes do not enter the diene synthesis (Diels-Alder reaction) or do so with considerable difficulty. Insofar as one of the alkyl groups in gem-substituted dienes is always in the cis-position, it was of considerable interest to study systematically their behavior in the reactions of diene synthesis.

There are but few scattered and often contradictory data in the literature bearing on this problem. Thus, for example, Bachmann [1] showed that 1,1-dimethylbutadiene does not form adducts with benzoquinone, maleic anhydride and crotonic acid even after prolonged heating at 200°. According to other work, 1,1-dimethylbutadiene [2-5] and 1,1,4-trimethylbutadiene [6] form only polymeric products with maleic anhydride. However, there is an entire series of patents [7-9] in which data are given about diene condensations of these dienes with various unsymmetric dienophiles (acrolein, metacrolein, crotonaldehyde and tetrolic aldehyde). Recently there also appeared some papers on diene condensations of 1,1-dimethylbutadiene with crotonaldehyde [5] and of 1,1,4,4-tetramethylbutadiene with tetrabromo-o-quinone [10]. In both cases the authors assumed the resulting compounds to be adducts with normal structure corresponding to Formulae (I) and (II).



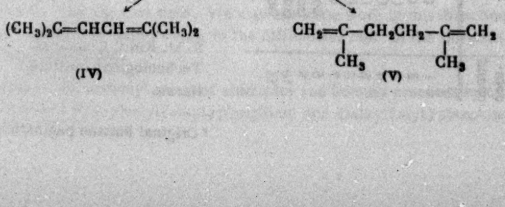
(I)



(II)

We selected 1,1-dimethyl-, 1,1,4-trimethyl- and 1,1,4,4-tetramethylbutadienes as gem-substituted dienes.

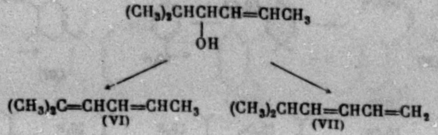
First of all we developed the accessible paths of preparation of 1,1,4,4-tetramethyl- and 1,1,4-trimethylbutadienes. In catalytic dehydration of tetramethyl-1,4-butanediol (III) over zirconium dioxide on pumice or over a catalyst composed of chromium oxide and aluminum oxide at 300° we obtained, in both cases with almost quantitative yield, the readily separable mixtures of 1,1,4,4-tetramethylbutadiene (IV) and 2,5-dimethyl-1,5-hexadiene (V) in approximately equal proportion.



$$(CH_3)_2\underset{OH}{C}CH_2CH_2\underset{OH}{C}(CH_3)_2 \quad \text{(III)}$$

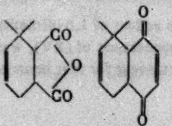
$$(CH_3)_2C{=}CHCH{=}C(CH_3)_2 \quad \text{(IV)} \qquad CH_2{=}\underset{CH_3}{C}{-}CH_2CH_2{-}\underset{CH_3}{C}{=}CH_2 \quad \text{(V)}$$

1,1,4-Trimethylbutadiene was prepared by us by dehydration of isopropylpropenylcarbinol over zirconium dioxide on pumice.



After a single pass at 290° there was obtained in 80% yield a mixture of hydrocarbons containing 60% of 1,1,4-trimethylbutadiene (VI) and 40% of 1-isopropylbutadiene (VII), while Bacon [3] by using hydrobromic acid obtained a hydrocarbon mixture with predominance of diene (VII).

The structure of dienes (IV), (VI) and (VII) was confirmed by a study of their oxidation products obtained with potassium permanganate. In addition to this, 1-isopropylbutadiene (VII) was characterized by crystalline derivatives which it formed with maleic anhydride and quinone (VIII) and (IX).



(VIII) (IX)

1,1,4,4-Tetramethyl- (IV), 1,1,4-trimethyl- (VI) and 1,1-dimethylbutadienes gave only amorphous polymeric products, which were evidently copolymers of the dienes and maleic anhydride, in reactions with maleic anhydride under various conditions (temperature, solvent, ratio of components, etc.).

The use of less reactive dienophiles (methyl acrylate, acrylonitrile, crotonaldehyde) for diene condensations requires the use of more drastic temperature conditions and in this case along with formation of large amounts of polymeric substances there are also formed adducts in yields of 15-30%. Thus, for example, 1,1,4,4-tetramethylbutadiene (IV) condensed only slightly with methyl acrylate at 200° and only after heating of the component mixture for five hours to 250-260° was there formed the adduct (X) in 20-30% yield, this adduct however, not being the normal adduct of a diene synthesis.

In the hydrolysis of the resulting adduct (X) we isolated a liquid acid (XI) which hydrogenated to acid (XII). The structure of the latter was established by dehydrogenation over the catalyst – chromium oxide on aluminum oxide, as well as palladium on carbon – and a subsequent oxidation of the dehydrogenation products with dilute nitric acid under pressure. Here we isolated only isophthalic acid from the oxidation products and not terephthalic acid which would have corresponded to the normal product of condensation of diene (IV) with methyl acrylate. This result was unexpected; it is necessary to assume that prior to the condensation there occurs a double transposition of the double bonds by a form of allylic shift with formation of a conjugated system with free methylene terminations,* i. e., the reaction proceeds through 1-isopropyl-3-methylbutadiene (XIII) formed from 1,1,4,4-tetramethylbutadiene (IV), the former substance entering the reaction of diene condensation in the normal manner.

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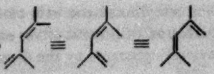
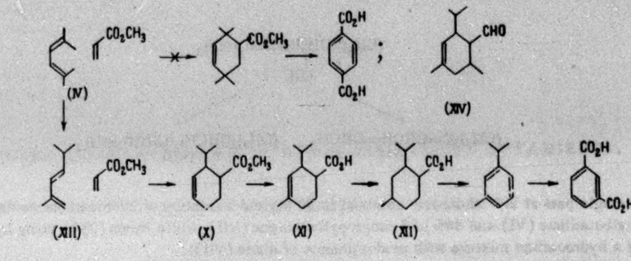
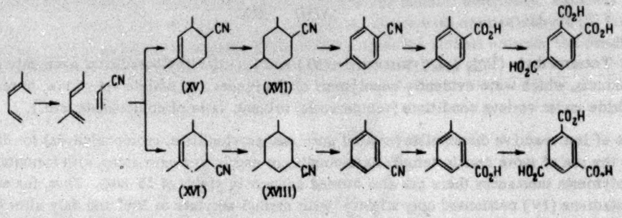
*In a recent review Alder and Schumacher [11] exclude the possibility of entry of all gem-substituted dienes into diene synthesis without an isomerization, with the exception made for 1,1,3-trimethylbutadiene, for which such a rearrangement leads to the same diene, i. e.,  (see structures, top of p. 3092).

Unfortunately the authors cite their own but unpublished material.



We isolated the unsaturated aldehyde (XIV), which evidently corresponds also to the adduct of the isomeric form of the diene (IV) and crotonaldehyde, from the condensation of 1,1,4,4-tetramethylbutadiene (IV) with crotonaldehyde, just as in the preceding instance. Similarly to this, 1,1-dimethylbutadiene isomerizes into 1,3-dimethylbutadiene under the conditions of the diene synthesis.

An adduct, which corresponds to the adduct of 1,3-dimethylbutadiene consisting of a mixture of structural isomers (XV) and (XVI) with a great preponderance of (XV), was formed in yields of about 20% by heating 1,1-dimethylbutadiene with acrylonitrile in a solvent for four hours at 200°.

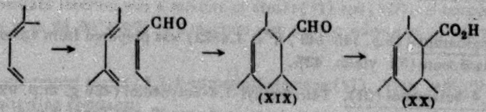


A considerable amount of decomposition of the adducts (up to 30%) occurs in the dehydrogenation of unsaturated nitriles (XV) and (XVI) over Cr_2O_3/Al_2O_3 even at 430° and, for this reason, we hydrogenated the latter prior to this operation.

The hydrogenation of the double bond over palladium catalyst proceeds very slowly, while over platinum oxide it is accompanied, at room temperature, by a partial reduction of the nitrile group.

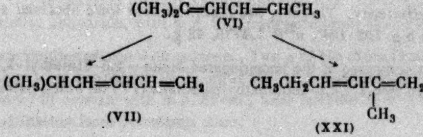
The mixture of saturated nitriles (XVII) and (XVIII) was transformed into aromatic nitriles, in yields of 30%, by passage over the Cr_2O_3/Al_2O_3 catalyst at 450°; after hydrolysis of the latter nitriles, we isolated 2,4-dimethylbenzoic acid. Dehydrogenation of the same mixture of nitriles over 20% palladium on carbon, followed by hydrolysis of the dehydrogenation products, gave a good yield of a mixture of aromatic acids, from which only 2,4-dimethylbenzoic acid could be isolated by recrystallization. The remaining mixture of acids (about 20%) was oxidized with dilute nitric acid, yielding a 3:1 ratio of trimellitic and trimesic acids. The presence of trimesic acid indicated the presence of the "meta" isomer in the reaction mixture, this isomer being (XVI), whose formation had been indicated earlier, as in the condensation of 1,3-dimethylbutadiene with acrylonitrile. The same result was obtained by running the reaction at a lower temperature (180°).

The condensation of 1,1-dimethylbutadiene with crotonaldehyde run for ten hours at 150° gave a 17-25% yield of adduct (XIX), whose oxidation with moist silver oxide gave mainly 2,4,6-trimethyl-Δ^3-tetrahydrobenzoic acid (XX), which had been previously prepared by the direct synthesis in the condensation of 1,3-dimethylbutadiene with crotonaldehyde [12].



Thus, the diene condensations of 1,1-dimethyl- and 1,1,4,4-tetramethylbutadienes proceed through a preliminary isomerization of the dienes into 1,3-dimethyl- and 1-isopropyl-3-methylbutadienes, respectively.

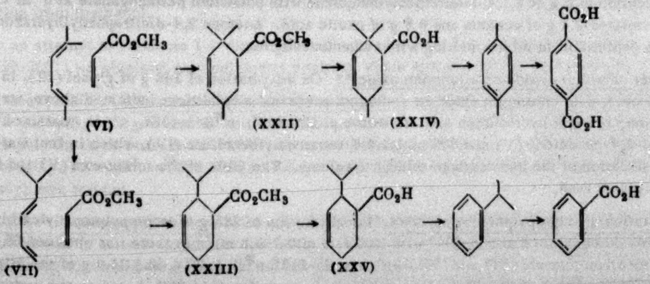
It was of interest to study, in this connection, the behavior of 1,1,4-trimethylbutadiene (VI), for which the rearrangement of this type should lead to formation of two isomeric forms of dienes (VII) and (XXI).



$$(CH_3)_2C{=}CHCH{=}CHCH_3 \quad \text{(VI)}$$

$$(CH_3)CHCH{=}CHCH{=}CH_2 \quad \text{(VII)} \qquad CH_3CH_2CH{=}CH\underset{\substack{|\\ CH_3}}{C}{=}CH_2 \quad \text{(XXI)}$$

The formation of two isomeric esters (XXII) and (XXIII) actually did occur during heating of 1,1,4-trimethylbutadiene (VI) with methyl acrylate for eight hours at 210°; the yields were 14-17% and the structures of the products were proven by the following series of reactions:



In this case we isolated from the reaction products mainly the terephthalic acid, which corresponds to the normal addition product, along with 20% of benzoic acid, which could form only from ester (XXIII) which corresponds to the isomeric form of the diene (VII).

The condensation of 1,1,4-trimethylbutadiene (VI) with crotonaldehyde for five hours at 220° gave a 15% yield of the unsaturated aldehyde (XXVI), which was identified by its 2,4-dinitrophenylhydrazone. We ran a condensation of 1-isopropylbutadiene with crotonaldehyde for comparison. By heating the mixture of these substances for seven hours at 170°, we obtained a 65% yield of aldehyde (XXVII), whose 2,4-dinitrophenylhydrazone was different from the one described above; therefore, aldehydes (XXVI) and (XXVII) were not identical.

Thus, the diene condensations of 1,1,4-trimethylbutadiene proceed with but a partial isomerization of the diene, in contrast to those of 1,1-dimethyl- and 1,1,4,4-tetramethylbutadienes, and despite the presence of the geminal groups, 1,1,4-trimethylbutadiene can form adducts with normal structure.

EXPERIMENTAL

1,1-Dimethylbutadiene (b.p. 75.8-76.2° at 725 mm, $n^{20}D$ 1.4542) was prepared by pyrolysis of isopropylvinylcarbinyl acetate.

Isopropylpropenylcarbinol (b.p. 146-149°, $n^{17}D$ 1.4322) was prepared from crotonaldehyde and isopropyl bromide by the Grignard route [3]; yield: 43%.

Tetramethyl-1,4-butanediol (III). Tetramethyl-1,4-butynediol (426 g, m.p. 92-94°), prepared by the condensation of acetone with acetylene, was hydrogenated over 30 g of Raney nickel in an autoclave in solution in 500 ml of alcohol. The hydrogenation was run at 40-45° with initial hydrogen pressure of 120 atmospheres. Theoretical amount of hydrogen (67.5 liters) was absorbed over three hours. From the reaction we obtained 380 g of tetramethyl-1,4-butanediol (III) with m.p. 91-92° (from petroleum ether).

Dehydration of tetramethyl-1,4-butanediol (III). a) Over zirconium dioxide on pumice.* By dehydration of 146 g of glycol (III), in solution in 100 ml of methyl alcohol, over zirconium dioxide on pumice (tube diameter 22 mm, length of catalyst layer 55 cm) in nitrogen stream at 300-310° and at the feed rate of 0.9-1.0 ml/min we obtained 104 g of a mixture of hydrocarbons (IV) and (V) with b.p. 120-134°, $n^{22}D$ 1.4346. The yield was 94%, based on the glycol used. The resulting mixture of hydrocarbons was distilled through a column with 39 theoretical-plate-efficiency. Thereby, two main fractions were obtained as follows: 1st b.p. 112-114°. $n^{23}D$ 1.4298, 53 g, and 2nd b.p. 132-134°, $n^{21}D$ 1.4776, 42 g.

The first fraction was composed of the unconjugated diene – 2,5-dimethyl-1,5-hexadiene (V) [13]. The latter was readily isomerized into 1,1,4,4-tetramethylbutadiene (IV) on being passed over the catalyst CrO_3/Al_2O_3 at 250° [13].

The second fraction was 1,1,4,4-tetramethylbutadiene (IV) which after a second distillation through a column with 39 theoretical-plate-effectiveness had the following constants:

B.p. 133.5-134° (762 mm), m.p. 12-13°, $n^{20}D$ 1.4783, d^{20}_4 0.7624. MR_D 40.94; calculated 38.21.

λ_{max} 243 mμ, ϵ_{max} 22,900 (heptane).

On oxidation of 5 g of 1,1,4,4-tetramethylbutadiene with potassium permanganate at 0° in the usual manner, we isolated 2.4 g of acetone and 0.8 g of oxalic acid. Acetone 2,4-dinitrophenylhydrazone and oxalic acid gave no depressions in mixed melting with authentic samples.

b) Over chromium oxide on aluminum oxide.** On dehydration of 146 g of glycol (III), in solution of 100 ml of alcohol, over chromium oxide on aluminum oxide under conditions indicated above, we obtained, after two passes, 105 g of hydrocarbon mixture with b.p. 122-132°, $n^{23}D$ 1.4564, which contained 45% of 2,5-dimethyl-1,5-hexadiene (V) and 55% of 1,1,4,4-tetramethylbutadiene (IV), which in fact was established by fractional distillation of the hydrocarbons through a column. The yield of the mixture of (V) and (IV) was 95% based on the glycol used.

Dehydration of isopropylpropenylcarbinol. In dehydration of 285 g of isopropylpropenylcarbinol over 20% zirconium dioxide on pumice at 285-290° with feed rate of 0.7-0.8 ml/min there was obtained 38 ml of water, 192 g of hydrocarbon mixture (VI) and (VII) with b.p. 95-112°, $n^{20}D$ 1.4514, and 34.0 g of the original carbinol with b.p. 138-150°, $n^{20}D$ 1.4292. Thus, the yield of the hydrocarbons was 80%, based on the carbinol used, or 91%, based on the amount of converted carbinol. The resulting hydrocarbon mixture was fractionated through a column of 39 theoretical-plate-effectiveness, in the presence of metallic sodium. The following main fractions were obtained: 1st b.p. 89-92°, $n^{22}D$ 1.4355, 51.4 g, 2nd b.p. 92-109°, $n^{22}D$ 1.4504, 16.0 g, and 3rd b.p. 109-111°, $n^{22}D$ 1.4648, 92.0 g.

The first fraction was shown to be 1-isopropylbutadiene, after repeated distillation. This (VII) had the following constants:

B.p. 90-91° (744 mm), $n^{20}D$ 1.4358, λ_{max} 225 mμ, ϵ_{max} 21,000 (heptane).
Found %: C 87.23, 87.18; H 12.46, 12.62. C_7H_{12}. Calculated %: C 87.42; H 12.58.

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* Preparation of this catalyst was described in our preceding paper.

** This catalyst was prepared by the method described by Levina [14].

Isobutyric acid 1.4 g, whose p-bromophenacyl ester melted at 75-76° and gave no depression with an authentic specimen, was isolated by oxidation of 3 g of this diene with permanganate.

The second intermediate fraction was a mixture of dienes (VI) and (VII). A sample of this fraction gave a crystalline adduct with m.p. 89-90° (20%) in a reaction with maleic anhydride, in addition to some 70% of polymer.

The third fraction contained mainly 1,1,4-trimethylbutadiene (VI). This, redistilled through a fractionating column, had the following constants:

B.p. 110.3-110.6° (749 mm), $n^{20}D$ 1.4682, $d^{20}{}_4$ 0.7552, MR_D 35.25; calculated 33.59; λ_{max} 235.5 mμ, ϵ_{max} 24,000 (heptane).
Literature data: b.p. 111.5°, $n^{20}D$ 1.4680, $d^{20}{}_4$ 0.7449 [6].

Oxidation of 5 g of 1,1,4-trimethylbutadiene with potassium permanganate gave 1.45 g of acetone, 1.2 g of oxalic acid and 1.0 g of acetic acid.

Condensation of 1-isopropylbutadiene with maleic anhydride. Two g of the diene (b.p. 90-91°), 2 g of freshly sublimed maleic anhydride and 20 ml of benzene were heated, in the presence of pyrogallol, in a glass ampule for 12 hours at 100°. The reaction product was precipitated with petroleum ether. 3.5 g (86%) of 3-isopropyl-Δ^4-tetrahydrophthalic anhydride, with m.p. 91° (from petroleum ether) was obtained [3].

Condensation of 1-isopropylbutadiene with quinone. Two g of the diene (b.p. 90-91°), 2.2 g of benzoquinone and 20 ml of benzene were heated for 12 hours at 100° in a glass ampule. The solvent was distilled under vacuum and 2.9 g (64%) of crystals with m.p. 82-85°, were isolated from the residue. The adduct (IX) melted at 92° after recrystallization from petroleum ether.

Found %: C 76.01, 76.14; H 7.94, 7.87. $C_{13}H_{16}O_2$. Calculated %: C 76.43; H 7.89.

Condensation with maleic anhydride. 1) 1,1,4,4-Tetramethylbutadiene (2.2 g; b. p. 133-134°) and 6 g (3-fold excess) of maleic anhydride were heated under a reflux condenser for ten hours at 150°. The product was hydrolyzed with 40% solution of potassium hydroxide and then was acidified with concentrated hydrochloric acid. An abundant amorphous precipitate formed (5.0 g); the latter melted at 215-220° (with decomposition) after reprecipitation from methanol.

2) In an attempt to condense 1,1-dimethylbutadiene, as well as 1,1,4-trimethylbutadiene, with maleic anhydride (20-100°) we obtained only polymeric products, which agreed with the literature data [2].

Condensation of 1,1,4,4-tetramethylbutadiene with methyl acrylate. a) 1,1,4,4-Tetramethylbutadiene (22.5 g, $n^{24}D$ 1.4763), 17.2 g of methyl ester of acrylic acid (b.p. 80°) and 0.2 g of hydroquinone were heated in a steel ampule for three hours at 215-220°. After distillation of the reaction product we obtained 15 g of the original diene (b.p. 130-135°, $n^{28}D$ 1.4738), 3.5 g of adduct (X) (b.p. 101-108° at 7 mm, $n^{27}D$ 1.4635) and 10.5 g of polymeric residue.

b) 1,1,4,4-Tetramethylbutadiene (22.5 g), 19.0 g (10% excess) of methyl acrylate and 0.2 g of hydroquinone were heated in a steel ampule for four hours at 250-260°. After a vacuum distillation we obtained, besides the starting materials, 13 g (30%) of adduct (X) with b.p. 105-115° at 7 mm, $n^{25}D$ 1.4652) and 10.2 g of a high boiling fraction (b.p. 115-180° at 7 mm, $n^{25}D$ 1.4742) as well as 11.0 g of polymeric residue. After two distillations of the combined fractions which corresponded to the adduct, there was isolated 12 g of ester (X) with b.p. 95-99° (5 mm), $n^{23}D$ 1.4652.

A satisfactory analysis of the substance could not be obtained.

Hydrolysis of ester (X). Twelve g of the substance (b.p. 95-99° at 5 mm) was refluxed in 100 ml of 15% sodium hydroxide solution for 15 hours. The reaction product was extracted with ether for the removal of neutral product. The residue was acidified with concentrated hydrochloric acid (31 ml) and the separated oil was extracted with ether. The ethereal extract was dried with sodium sulfate, ether was distilled from it and the residue was vacuum distilled. There was obtained 7.6 g of acid (XI) with b.p. 139-141° (6 mm), $n^{20}D$ 1.4795.

Found %: C 72.73, 72.67; H 10.11, 10.05. M (titration) 176, 179. $C_{11}H_8O_2$. Calculated %: C 72.48; H 9.95. M 182.

Hydrogenation of acid (XI). Five g of the acid (b.p. 139-141° at 6 mm) was hydrogenated in a solution of 50 ml of acetic acid over platinum catalyst. In six hours there was absorbed the theoretical volume of hydrogen (600 ml). There was obtained 4.1 g of acid (XII) with b.p. 116-118° (1.6 mm), $n^{20}D$ 1.4726.

Dehydrogenation of acid (XII) and oxidation of resulting products. a) Eight g of substance was passed over the catalyst Cr_2O_3/Al_2O_3 * at 480° in a stream of nitrogen at the rate of a drop per 4-6 seconds. There was obtained 2.2 g of hydrocarbon (b.p. 138-172°, $n^{24}D$ 1.5012) which was then oxidized with 80 ml of 10% nitric acid [16] under nitrogen pressure of 25 atmospheres at 200° over two hours. After separation of the resulting acid through the barium salt [17], we isolated 1.2 g of isophthalic acid with m.p. above 250°, whose dimethyl ester melted at 64° and gave no depression in mixed melting point with an authentic specimen. No terephthalic acid could be isolated.

b) Four g of the substance was dehydrogenated over 20% palladium on carbon over 3 hours. We obtained 2.0 g of a hydrocarbon ($n^{19}D$ 1.5021), upon oxidation of which and separation, as described above, we obtained only isophthalic acid (1 g). The mixed melting point of its dimethyl ester gave no depression with an authentic sample.

Condensation of 1,1,4,4-tetramethylbutadiene with crotonaldehyde. The diene (22.5 g, b.p. 133-134°), 14 g of crotonaldehyde (b.p. 101-103°), 40 ml of benzene and 0.2 g of pyrogallol were heated in a steel ampule for five hours at 230°. After three redistillations of the reaction product in vacuum there was isolated 5.4 g of unsaturated aldehyde (XIV) with b. p. 85-88° (4 mm), $n^{20}D$ 1.4758, and 12 g of polymeric residue. The 2,4-dinitrophenylhydrazone of the aldehyde melted at 145° (from alcohol).

Found %: C 60.10, 60.32; H 6.89, 6.74; N 15.42, 15.62. $C_{18}H_{24}O_4N_4$. Calculated %: C 60.00; H 6.68; N 15.52.

Condensation of 1,1-dimethylbutadiene with acrylonitrile. a) Thirty g of the diene, 20 g of acrylonitrile, 20 ml of benzene and 0.2 g of hydroquinone were heated in a steel ampule for four hours at 200°. After two redistillations of the reaction product in vacuum we obtained 11.2 g (23%) of a mixture of nitriles (XV) and (XVI) with b.p. 76-81° (7 mm), $n^{20}D$ 1.4708-1.4721; polymeric residue – 24 g.

Found %: C 80.54, 80.35; H 9.96, 9.74. $C_9H_{13}N$. Calculated %: C 80.0; H 9.68.

b) Ten g of the diene, 6.7 g of acrylonitrile and hydroquinone were heated at 140° for 15 hours. After distillation of the reaction product in vacuum there was obtained 2.8 g of a substance with b.p. 91-96° (14 mm), $n^{19.5}D$ 1.4692; polymeric residue: 10 g.

Hydrogenation of the mixture of adducts (XV) and (XVI). The mixture of nitriles obtained above (14.3 g) was hydrogenated in a solution of 50 ml of alcohol over platinum catalyst at room temperature. Over 15 hours 2320 ml of hydrogen was absorbed (2360 ml required at 18°, 746 mm). For the removal of the resulting amine, the reaction product was acidified with 10% hydrochloric acid and extracted with ether. The ether was distilled and the residue was vacuum distilled. There was obtained 9.2 g of a mixture of saturated nitriles (XVII) and (XVIII) with b.p. 85-88° (12 mm), $n^{19}D$ 1.4580.

Found %: N 9.74, 9.87. $C_9H_{15}N$. Calculated %: N 10.20.

Dehydrogenation and hydrolysis of mixture of nitriles (XVII) and XVIII). a) Six g of the substance (b.p. 85-88° at 12 mm) was dehydrogenated over Cr_2O_3/Al_2O_3 at 480° in a stream of nitrogen. After three passes there was obtained 1.8 g (30%) of aromatic nitriles ($n^{18}D$ 1.5018). The resulting dehydrogenation product was hydrolyzed with a mixture of 5 g of potassium hydroxide in 9 ml of alcohol and 0.5 ml of water by heating for 20 hours at 140°. The reaction product was acidified with concentrated hydrochloric acid and the precipitated crystals were separated and recrystallized from 40% methanol. There was obtained 0.8 g of 2,4-dimethylbenzoic acid with m.p. 126-127°, which did not give a depression with an authentic specimen.

b) Five g of the substance was dehydrogenated over 20% palladium on carbon at 320° over 2.5 hours. There was obtained 3.8 g of aromatic nitriles with b.p. 106-109° (20 mm), $n^{23}D$ 1.5208. The latter were hydrolyzed with a mixture of 8 g of potassium hydroxide in 13 ml of alcohol and 0.8 ml of water by heating for 25 hours at 140°. We obtained 3.0 g of a mixture of dimethylbenzoic acids, by the recrystallization of which we

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* This catalyst was prepared by the method described by Ferrin [15].

isolated 2.1 g of 2,4-dimethylbenzoic acid with m.p. 126°, which did not give a depression with an authentic specimen. The remainder (0.6 g), with m.p. 82-96°, was oxidized with 50 ml of 10% nitric acid under nitrogen pressure of 30 atmospheres at 200° over two hours. We obtained 0.5 g of a mixture of trimesic and trimellitic acids. By recrystallization from 10% hydrochloric acid, we obtained 0.25 g of trimellitic acid with m.p. 224-227°, which did not give a depression with an authentic specimen. In addition there was obtained 0.16 g of trimesic acid with m.p. above 260°, whose trimethyl ester melted at 144° and did not give a depression with an authentic specimen.

Condensation of 1,1-dimethylbutadiene with crotonaldehyde. 1,1-Dimethylbutadiene (15 g), 12.5 g of crotonaldehyde, 25 ml of petroleum ether and 0.1 g of hydroquinone were heated for 14 hours at 145-150°. After two redistillations of the reaction product in vacuum there was isolated 6.2 g of adduct (XIX) with b.p. 85-90° (16 mm), $n^{18}D$ 1.4732.

Found %: C 78.91, 78.96; H 10.2, 10.34. $C_{10}H_{16}O$. Calculated %: C 78.95; H 10.53.

Semicarbazone of aldehyde (XIX) melts at 182-183° (from alcohol). A mixed melting point with semicarbazone of 2,4,6-trimethyl-Δ^3-tetrahydrobenzaldehyde (m.p. 183°), prepared by condensation of 1,3-dimethylbutadiene with crotonaldehyde [12], gave no depression.

Oxidation of aldehyde (XIX). To the previously prepared moist silver oxide (from 8.7 g of silver nitrate and 120 ml of 0.5 N potassium hydroxide solution) was added 3.8 g of the substance (b.p. 85-90° at 16 mm) and 3 g of potassium hydroxide in a solution of 125 ml of 50% alcohol and the mixture was shaken at room temperature for 25 hours. The precipitate was filtered off, the filtrate was evaporated in vacuum to a small volume, acidified with concentrated hydrochloric acid and the separated oil was extracted with ether. On distillation 2.4 g of acid (XX) with b.p. 124-128° (3.5 mm) was obtained, which crystallized almost completely on standing and melted at 97-98° (from 30% methanol). A sample mixed with 2,4,6-trimethyl-Δ^3-tetrahydrobenzoic acid gave no melting point depression.

Condensation of 1,1,4-trimethylbutadiene with methyl acrylate. 1,1,4-Trimethylbutadiene (19.2 g, b.p. 110.5°, $n^{20}D$ 1.4672), 18 g (10% excess) of methyl ester of acrylic acid and 0.1 g of hydroquinone in a solution of 40 ml of petroleum ether were heated in a steel ampule at 200° for ten hours. After distillation in vacuum we obtained, besides the starting materials, 6.3 g of a mixture of esters (XXII) and (XXIII) with b.p. 75-82° (8 mm), b.p. 88-90° (11 mm), $n^{20}D$ 1.4535. Polymeric residue: 10 g.

Found %: C 72.18, 71.93; H 9.86, 9.78. $C_{11}H_{18}O_2$. Calculated %: C 72.49; H 9.96.

Hydrolysis of the mixture of adducts (XXII) and (XXIII). The substance (4.5 g, b.p. 88-90° at 11 mm) was boiled with 30 ml of 20% solution of sodium hydroxide for ten hours. The reaction product was extracted with ether, the aqueous layer was acidified with concentrated hydrochloric acid (14 ml) and the separated oil was extracted with ether. The ethereal extract was dried over magnesium sulfate, the ether was distilled from it and the residue was vacuum distilled. There was obtained 3.8 g of a mixture of acids (XXIV) and (XXV) with b.p. 113-115° (2 mm), $n^{21}D$ 1.4718.

Found %: C 71.25, 71.17; H 9.62, 9.55. M (titration) 163, 162. $C_{10}H_{16}O_2$. Calculated %: C 71.38; H 9.58. M 168.

After prolonged standing, from 1.8 g of the above mixture of acids we isolated 0.3 g of crystals with m.p. 92°.

Found %: C 70.97, 71.19; H 9.53, 9.47. $C_{10}H_{16}O_2$. Calculated %: C 71.38; H 9.58.

Dehydrogenation of mixture of acids (XXIV) and (XXV) and oxidation of the resulting products. Two g of the substance (b.p. 113-115° at 2 mm) was dehydrogenated over 20% palladium on carbon at 310° over 1.5 hours. There was obtained about 1.0 g of a mixture of hydrocarbons ($n^{19}D$ 1.4942). This mixture was oxidized with 45 ml of 8% nitric acid under nitrogen pressure of 30 atmospheres at 200° for two hours. The oxidation products were evaporated to a small volume and were thoroughly extracted with benzene. From the benzene extracts we obtained 60 mg of benzoic acid with m.p. 120-122°, which did not give a depression with an authentic specimen. From the residue after separation through the barium salts we isolated 0.4 g of terephthalic acid with m.p. above 260°, whose dimethyl ester melted at 144° and gave no depression in mixed melting with an authentic specimen. No isophthalic acid could be isolated in this case.

Condensation of 1,1,4-trimethylbutadiene with crotonaldehyde. 1,1,4-Trimethylbutadiene (26.0 g) 17.5 g of crotonaldehyde and 0.2 g of hydroquinone were heated in a solution of 40 ml of petroleum ether in a steel ampule for eight hours at 220-225°. After distillation of the reaction products in vacuum there was obtained besides the starting materials, 14.2 g of a substance with b.p. 70-140° (7 mm). Polymeric residue: 15.0 g. After numerous redistillations we isolated 4.8 g of a substance, with b.p. 70-80° (6 mm), $n^{20}D$ 1.4721 which corresponded to adduct (XXVI). On treatment of this adduct (XXVI) with a solution of 2,4-dinitrophenylhydrazine we isolated a 2,4-dinitrophenylhydrazone (about 22%) with m.p. 183° (from ethyl acetate).

Found %: C 58.64, 58.62; H 6.02, 6.25; N 16.36, 16.40. $C_{17}H_{22}O_4N_4$. Calculated %: C 58.93; H 6.40; N 16.14.

Condensation of 1-isopropylbutadiene with crotonaldehyde. Five g of 1-isopropylbutadiene (b.p. 90-91°), 3.5 g of crotonaldehyde and a little hydroquinone were heated in a steel ampule at 170° for seven hours. After a vacuum distillation we obtained 5.6 g (65%) of aldehyde (XXVII) with b.p. 84-86° (7 mm), $n^{20}D$ 1.4754. The semicarbazone of the aldehyde melted at 184-185° (from alcohol).

Found %: C 64.18, 64.24; H 9.51, 9.54; N 19.31, 19.08. $C_{12}H_{21}ON_3$. Calculated %: C 64.52; H 9.38; N 18.91.

2,4-Dinitrophenylhydrazone of the aldehyde had m.p. 165-167° (from alcohol).

Found %: N 16.35, 16.41. $C_{17}H_{22}O_4N_4$. Calculated %: N 16.14.

SUMMARY

1. A new and convenient method was developed for the preparation of 1,1,4,4-tetramethylbutadiene (diisocrotyl) by dehydration of tetramethyl-1,4-butanediol.

2. It was shown that a mixture of isomeric dienes, containing 60% 1,1,4-trimethyl and 40% 1-isopropylbutadienes, is formed in the catalytic dehydration of isopropylpropenylcarbinol over zirconium dioxide on pumice.

3. It was shown that 1,1,4,4-tetramethyl- and 1,1-dimethylbutadienes enter the diene synthesis (Diels-Alder reaction) only at high temperatures and undergo a preliminary isomerization into the corresponding 1,3-disubstituted dienes, while 1,1,4-trimethylbutadiene isomerizes only partially under these conditions and yields mainly the adduct with normal structure.

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REACTIONS OF HYDRAZINE DERIVATIVES

XX. DEHYDROGENATION OF PYRAZOLINES*

I. I. Grandberg and A. N. Kost

Pyrazolines have become readily available substances recently. It is possible to synthesize pyrazolines with various alkyl or aryl substituents in any desired position by: the reaction of α, β-unsaturated carbonyl compounds [1, 2] or β-amino ketones [3-5] with hydrazine, the cyclization of azines under the influence of acids [6] or the reaction of addition of aliphatic diazo compounds to carbon-carbon double bond [7].

All the pyrazolines are rather unstable in storage and, for this reason, many workers attempted to oxidize these substances to pyrazoles for identification, since the latter are distinguished by their chemical stability and by the fact, as it recently appeared, of their being fungicides [8], insecticides [9] and antibiotics [10].

The transformation of pyrazolines into pyrazoles turned out to be a difficult problem since these substances are easily oxidized, often with spontaneous ignition, by the action of plain atmospheric oxygen [11]. It was possible to prepare only saturated and unsaturated ketones and complex nitrogenous substances by slow oxidation of nitrogen-unsubstituted pyrazolines with hydrogen peroxide [12]. N-Phenylpyrazolines yield colored condensation products, whose structures remain undetermined, after careful oxidation [13]. It was possible in individual cases to oxidize a pyrazoline to a pyrazole, but in each case it was necessary to select the proper conditions and the specific oxidizing agent [14]. Bromine was used for this purpose in a series of papers; however, this reagent leads mainly to the bromination products [15].

Our attempts to oxidize 4-ethyl-5-propyl- and 4-isopropyl-5-isobutylpyrazolines to the corresponding pyrazoles were similarly unsuccessful. Performic acid, selenium dioxide, nitric acid, potassium permanganate, sodium dichromate and chromic anhydride all destroyed the pyrazoline ring, yielding a nitrogen-free complex mixture of oxidation products. Attempts to oxidize N-formyl-, N-acetyl- and N-benzoyl derivatives of these pyrazolines were similarly unsuccessful, since the weak oxidants failed to affect these compounds, while the stronger ones (potassium permanganate in all media and chromic acid) destroyed the pyrazolines with evolution of nitrogen. In the action of bromine on these pyrazolines and their acyl derivatives there took place a bromination along with the oxidation and there was formed a complex mixture of bromine-containing substances.

The smooth transition from pyrazolines to pyrazoles was attained by us by the use of selenium or, even better, sulfur, for the dehydrogenating agents. The reaction proceeds at a rather low temperature (150-250°) and is not accompanied by side reactions. The end of the reaction can be noted easily by the cessation of evolution of hydrogen sulfide. It is interesting to note that excess sulfur is not necessary for the reaction.

In pyrazoles, in contrast to pyrazolines, there exists a conjugation of two double bonds with free electron pairs of the nitrogen atom. In such an aromatized structure, having a sextet of electrons in the nucleus, the compounds with a substituent in position 3 were identical with analogous substances having the substituent in position 5. Owing to this, for example, in dehydrogenation of 3-methyl-5-phenylpyrazoline there was obtained 3-phenyl-5-methylpryazole in 90% yield. Analogously, from both 5-methyl- and 3-methylpyrazoline there was obtained the same 3(5)-methylpyrazole in yields of 75% and 90% respectively.

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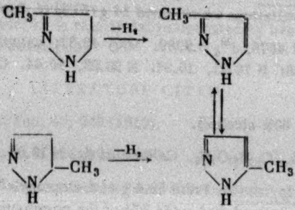
*Paper I from the series "Studies on Pyrazoles".



By dehydrogenation of pyrazolines in this manner we prepared a series of pyrazoles, in yields of 65 to 96%, among them four of the previously unknown ones. The proposed method may serve the purposes of preparative synthesis of alkyl- and arylpryrazoles, owing to the simplicity of the experiments and the comparative accessibility of the starting materials. In the example of synthesis of methylfurylpyrazole we established that this method may be used also for the more complex substances.

EXPERIMENTAL

One mole of pyrazoline, mixed with one mole of sulfur (selenium gave considerably lower yields), was heated until energetic evolution of hydrogen sulfide began (temperature of the mixture 150-250°). The reaction flask was then heated or slightly cooled (with a moist towel) so as to keep the reaction rate approximately constant (a very energetically going reaction leads to the appearance of tarry products). The rate of the reaction may be determined by the length of the flame of hydrogen sulfide if one ignites it at the end of the exit tube; in dehydrogenation of 0.2 mole of pyrazoline and with the diameter of the exit tube being 2.5 mm, the flame length was 2 cm. After termination of evolution of hydrogen sulfide (usually 30-60 minutes was required for this), the flask was heated for 20 minutes longer for the completion of the reaction.

In case of low-boiling alkylpyrazolines the reaction was run in a flask with a reflux condenser and after completion of the dehydrogenation the still hot reaction mixture was transferred into a Claisen flask and the pyrazole was vacuum distilled. Pyrazolines with phenyl substituents (which boiled from 300° and higher) can be dehydrogenated in a beaker made of thermostable glass and the resulting pyrazole can be directly recrystallized.

3(5)-Methylpyrazole. From 16.8 g of 5-methylpyrazoline (b.p. 150-151° at 741 mm, $n^{20}D$ 1.4781 [16]) we obtained 12.4 g (75%) of 3(5)-methylpyrazole with b.p. 202-205° (750 mm). After second distillation, the substance had the following constants:

B.p. 202-203° (747.5 mm), $n^{20}D$ 1.4928, d^{20}_4 1.0119 [17]. MR_D 23.59; calculated 23.88.[*]

Found %: N 34.07, 34.20. $C_4H_6N_2$. Calculated %: N 34.18.

Picrate (from ether), m.p. 142° [17].

From 16.8 g of 3-methylpyrazoline (b.p. 64-66° at 25 mm, $n^{20}D$ 1.4736 [5]) we obtained 15.1 g (90%) of 3-methylpyrazole; b.p. 202-203° (749 mm), $n^{20}D$ 1.4931, d^{20}_4 1.0131.

Picrate, m.p. 143° (from ether); gave no depression in mixed melting point with the picrate of the pyrazole prepared from 5-methylpyrazoline.

3(5)-tert-Butylpyrazole. From 25.2 g of 3-tert-butylpyrazoline (b.p. 66-68° at 9 mm, $n^{20}D$ 1.4670 [5]) we obtained 22.0 g (90%) of 3-tert-butylpyrazole with b.p. 106° (9 mm). On standing the product crystallized; m.p. 53° (from a small volume of petroleum ether).

Found %: C 68.13, 68.04; H 9.83, 9.80; N 22.41, 22.47. $C_7H_{12}N_2$. Calculated %: C 67.71; H 9.75; N 22.56.

Picrate, m.p. 141° (from 50% alcohol).

Found %: N 19.62, 19.78. $C_{13}H_{15}O_7N_5$. Calculated %: N 19.82.

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[*] The refraction value of 5.871 was taken for the two nitrogens in pyrazoles as in pyrazolines.

3(5)-Propyl-4-ethylpyrazole. From 28 g of 4-ethyl-5-propylpyrazoline (b.p. 101-103° at 16 mm, $n^{20}D$ 1.4674 [16]) after two distillations we obtained 14 g (51%) of 3-propyl-4-ethylpyrazole.

B.p. 133° (9 mm), $n^{20}D$ 1.4875, d^{20}_4 0.9389. MR_D 42.37; calculated 42.35.
Found %: C 69.30, 69.38; H 10.21, 10.37; N 20.28, 20.44. $C_8H_{14}N_2$. Calculated %: C 69.53; H 10.21; N 20.27.

Picrate, m.p. 142° (from 50% alcohol).

Found %: N 18.97, 19.05. $C_{14}H_{17}O_7N_5$. Calculated %: N 19.06.

3(5)-Isobutyl-4-isopropylpyrazole. From 50.4 g of 4-isopropyl-5-isobutylpyrazoline (b.p. 116-117° at 21 mm, $n^{20}D$ 1.4642 [16]) we obtained 32.1 g (64.5%) of the corresponding pyrazole.

B.p. 137° (9 mm), $n^{20}D$ 1.4749, d^{20}_4 0.9075. MR_D 51.57; calculated: 51.58.
Found %: C 71.98, 72.07; H 10.97, 10.91; N 16.91, 17.03. $C_{10}H_{18}N_2$. Calculated %: C 72.24; H 10.89; N 16.87.

Picrate, m.p. 69° (from 50% alcohol).

Found %: N 17.62, 17.69. $C_{16}H_{21}O_7N_5$. Calculated %: N 17.71.

3(5)-Phenylpyrazole. From 29.2 g of 5-phenylpyrazoline (b.p. 132-133° at 10 mm [1]) we obtained 22.9 g (78.8%) of 3-phenylpyrazole with b.p. 189-196° (20 mm) [18] in the form of a viscous oil which crystallized in the condenser and melted at 79° (from a mixture of benzene and isooctane in 1 : 3 ratio) [19].

Found %: N 19.43, 19.64. $C_9H_8N_2$. Calculated %: N 19.43.

Picrate, m.p. 170° (from ether) [18].

Found %: N 18.91, 19.17. $C_{15}H_{11}O_7N_5$. Calculated %: N 18.76.

The same pyrazole was obtained in 87% yield from dehydrogenation of 3-phenylpyrazoline (b.p. 142-143° at 9 mm, m.p. 44° [20]). B.p. 185-189° (15 mm), m.p. 79°.

Picrate, m.p. 170° (from ether). This gave no depression in mixed melting point with the picrate described above.

3-Methyl-5-phenylpyrazole. From 32 g of 3-methyl-5-phenylpyrazoline we obtained 27.9 g (89%) of 3-methyl-5-phenylpyrazole, m.p. 127° (from a mixture of octane-benzene in 1 : 1 ratio) [19].

Found %: N 17.82, 17.98. $C_{10}H_{10}N_2$. Calculated %: N 17.70.

Picrate, m.p. 158° (from ether) [21].

Found %: N 17.85, 17.92. $C_{16}H_{13}O_7N_5$. Calculated %: N 18.06.

3,5-Diphenylpyrazole. From 25 g of 3,5-diphenylpyrazolidine [22] we obtained 23.8 g (96%) of 3,5-diphenylpyrazole with m.p. 205° (from methyl alcohol) [23].

Found %: N 12.70, 12.74. $C_{15}H_{12}N_2$. Calculated %: N 12.49.

Picrate, m.p. 163° (from ether) [24].

Found %: N 15.57, 15.70. $C_{21}H_{15}O_7N_5$. Calculated %: N 15.48.

3-Methyl-5-(2-furyl)-pyrazole. Sixteen g of 3-methyl-5-(2-furyl)-pyrazoline was heated with 3.43 g of sulfur. After distillation there was isolated 11.1 g (70%) of methylfurylpyrazole with b. p. 167-176° (18 mm). The substance crystallized in the receiver. M. p. 90° (from a mixture of iso-octane-benzene in 4 : 1 ratio).

Found %: N 18.98, 19.05. $C_8H_{10}ON_2$. Calculated%: N 18.90.

Picrate, m.p. 132-133° (from 40% alcohol).

Found %: N 18.61, 18.63.* $C_{14}H_{11}O_8N_5$. Calculated %: N 18.56.

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* Nitrogen analyses were done by L. S. Ignatenko to whom the authors express their gratitude.

SUMMARY

It was shown that the pyrazoline nucleus is readily dehydrogenated by heating with sulfur. A method of synthesis of pyrazoles in high yields was developed.

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ADDITION OF ORGANOMAGNESIUM COMPOUNDS TO ISOPROPYLIDENEMALONIC ESTER

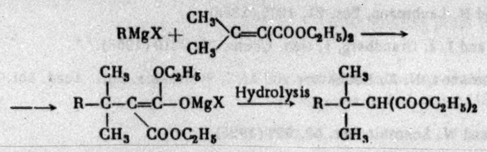
V. P. Gol'mov and Z. P. Malevannaia

Substituted malonic esters are formed in very poor yields in the reaction of the sodiomalonic ester with tertiary alkyl halides, since in this case there occurs a series of side-reactions (such as loss of the elements of hydrogen halide, formation of ethers, etc.) [1].

Therefore, another method of preparation of these compounds, consisting of the addition of organomagnesium compounds to alkylidenemalonic esters, deserved some attention.

This reaction was discovered as long ago as 1905 [2, 3] but it was used to this time on only a limited number of examples [4-11].

In order to partly fill this gap, we decided to study in this work the addition of some organomagnesium compounds to isopropylidenemalonic ester, which, as shown by the previous experiments with methylmagnesium iodide [4], butylmagnesium bromide [4], phenylmagnesium bromide [6] and benzylmagnesium bromide [6], proceeds according to the following scheme:



$$RMgX + (CH_3)_2C{=}C(COOC_2H_5)_2 \longrightarrow R{-}C(CH_3)_2{-}C(COOC_2H_5){=}C(OC_2H_5){-}OMgX \xrightarrow{\text{Hydrolysis}} R{-}C(CH_3)_2{-}CH(COOC_2H_5)_2$$

Some experiments are described below, dealing with the addition of organomagnesium compounds to isopropylidenemalonic ester, the former being prepared from ethyl iodide, propyl bromide, isopropyl bromide and butyl bromide.

We obtained in each case the expected tert-alkylmalonic esters, the hydrolysis of which gave tert-alkylmalonic acids, whose decarboxylation gave tert-alkylacetic acids.

EXPERIMENTAL

The isopropylidenemalonic ester, which is necessary for the following experiments, was prepared by the method of Gaind and Guha [12] and that of Cope and Hancock [13], from the malonic ester and acetone, in the presence of acetic anhydride and zinc chloride.

It had the following constants after careful distillation through a 20 cm Vigreaux column:

B.p. 79-80° (at 2 mm), d^{17}_4 1.0283 [14], d^{20}_4 1.0263, $n^{17}D$ 1.4514 [14], $n^{20}D$ 1.4490.

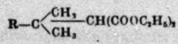
Addition of alkylmagnesium halides to isopropylidenemalonic ester. The Grignard reagent was prepared, in a flask provided with a reflux condenser, a mechanical stirrer and a dropping funnel, from 0.5 mole of alkyl halide in 200 ml of absolute ether and 0.5 gram-atom of metallic magnesium, activated by addition of iodine.

Isopropylidenemalonic ester (0.5 mole), dissolved in an equal volume of ether, was added dropwise with cooling and mechanical stirring, to the resulting solution of the organomagnesium compound. After the addition, the reaction mixture, which consisted of two layers, was set aside overnight at room temperature, after which it was refluxed for one hour on a water bath, cooled and decomposed with 150 ml of 1:1 hydrochloric acid. A crystalline mass precipitated at first, then redissolved on continued addition of the hydrochloric acid.

The ethereal layer was separated and the aqueous layer was extracted with ether; the combined ethereal layers were washed with sodium sulfite solution, with water, and then were dried over dried sodium sulfate; ether was then distilled off. The residue was fractionated under vacuum whereupon a fraction consisting of isopropylmalonic ester (formed by reduction of the isopropylidenemalonic ester) came over first, followed by the addition product which was then further purified by repeated vacuum distillations. A considerable amount of tar remained in the flask.

TABLE 1

Alkylmalonic Esters

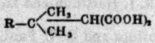


$R-C(CH_3)_2-CH(COOC_2H_5)_2$

R	Boiling point (pressure in mm)	Yield (in %)	n_D^{20}	d_4^{20}	MR_D		% C		% H	
					found	calc.	found	calc.	found	calc.
C_2H_5	92° (3)	36.8	1.4320	0.9831	60.92	60.55	62.34	62.61	9.57	9.57
C_3H_7	88—89 (1.5)	31.6	1.4352	0.9733	65.61	65.54	63.73	63.93	9.77	9.84
iso-C_3H_7	84 (1.5)	14.6	1.4394	0.9913	64.86	65.54	63.46	63.93	9.77	9.84
C_4H_9	119 (4)	30.5	1.4365	0.9580	70.06	70.16	65.31	65.12	10.16	10.08

TABLE 2

Substituted Malonic Acids

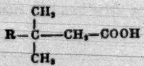


$R-C(CH_3)_2-CH(COOH)_2$

R	Melting point	% C		% H	
		found	calc.	found	calc.
C_2H_5	120—121°	55.02	55.17	8.17	8.05
C_3H_7	113—114	57.34	57.44	8.70	8.51
iso-C_3H_7	128—129.5	57.51	57.44	8.62	8.51

TABLE 3

Alkylacetic Acids



$R-C(CH_3)_2-CH_2-COOH$

R	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}	MR_D		%C		%H	
				found	calc.	found	calc.	found	calc.
C_2H_5	87—88° (5)	1.4238	0.9246	35.86	36.06	64.44	64.62	10.86	10.77
C_3H_7	98 (5)	1.4307	0.9157	40.65	40.68	66.53	66.67	11.25	11.11
iso-C_3H_7	98—99 (5)	1.4356	0.9302	40.44	40.68	66.48	66.67	11.18	11.11

The yields, constants and the analytical results of these compounds prepared by us are given in Table 1.

The tert-alkylmalonic esters were hydrolyzed with alcoholic alkali and the substituted malonic acids formed in this manner (Table 2) were changed to the tert-alkylacetic acids by heating to 180°. The properties of the latter are given in Table 3.

SUMMARY

1. Addition of ethylmagnesium iodide, propylmagnesium bromide, isopropylmagnesium bromide and butylmagnesium bromide to isopropylidenemalonic ester was examined.

2. The previously undescribed α,α-dimethylpropylmalonic, α,α-dimethylbutylmalonic and α,α,β-trimethylpropylmalonic esters were synthesized.

3. By hydrolysis of the indicated malonic esters there were prepared the corresponding tert-alkylmalonic acids, and by decarboxylation of the latter there were prepared 3,3-dimethylpentanoic, 3,3-dimethylhexanoic and 3,3,4-trimethylpentanoic acids.

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TRIAMINOPYRIDOTHIAZOLE AND THE PRODUCTS OF ITS CONDENSATION WITH DICARBONYL COMPOUNDS

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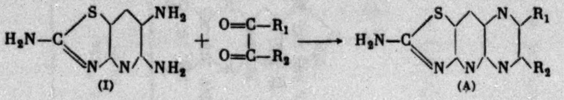
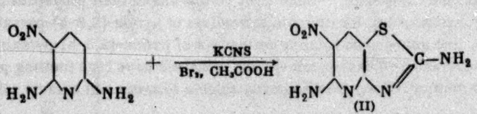
In our previous papers we described the synthesis of derivatives of pyrido-[4,3-d]-thiazole [1], pyrido-[3,2-d]-thiazole [2], pyrido-[2,3-d]-thiazole [3, 4]. The aim of the present work was the synthesis of the previously undescribed 2,5,6-triaminopyrido-[2,3-d]-thiazole (I), its condensation with dicarbonyl compounds and the clarification of physiological activity of the resulting compounds. The condensation products of this triamine with α-dicarbonyl compounds – pyrazino-[5,6-b]-pyrido-[2,3-d]-thiazoles (A) represent a complex condensed system of nitrogenous heterocycles.

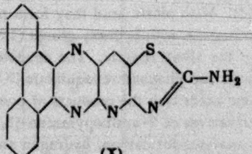


They may be regarded structurally as pteridine-like compounds in which the pyrimidine nucleus of the pteridine system was replaced by a pyridothiazole residue.

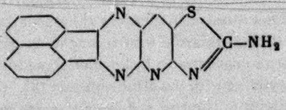
The initial 2,5,6-triaminopyrido-[2,3-d]-thiazole was synthesized by us in the following manner: 2,6-diamino-3-nitropyridine, described previously [5], was transformed into 2,5-diamino-6-nitropyrido-[2,3-d]-thiazole (II) by the thiocyanation reaction.



We prepared triaminopyridothiazole (I) in good yield by reduction of (II) with iron filings in aqueous alcoholic solution in the presence of acetic acid. The substance (I) was identified also as a dihydrochloride, a sulfate and a triacetyl derivative. For proof of the presence of two amino groups in ortho-position, the condensation products of base (I) with phenanthrenequinone (X) and with acenaphthoquinone (XI) were prepared.

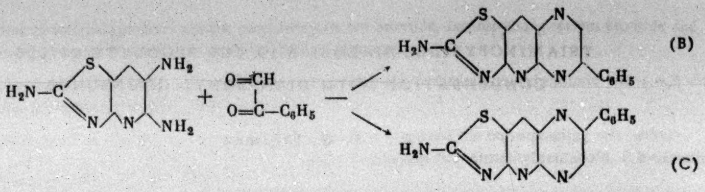


(X)

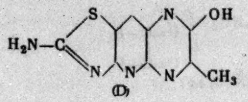


(XI)

Condensation with symmetric dicarbonyl compounds led to the formation of derivatives of 2-aminopyrazino-[5,6-b]-pyrido-[2,3-d]-thiazole (A, $R_1 = R_2$). Their structure does not present any doubt. In condensation with unsymmetric dicarbonyl compounds, such as pyruvic acid and phenylglyoxal, the formation of two isomers is possible. Thus, in the condensation with phenylglyoxal there may form bases in which the phenyl radical is either in 6 position (B) or in 7 position (C).



Starting with this fact that the amino group in 3-position of the pyridine nucleus is more reactive than an amino group in 2-position, it is possible to consider that the thiazole (B) should be the predominant compound in the condensation product of 2,5,6-triaminopyrido-[2,3-d]-thiazole with phenylglyoxal. Analogously it is possible to consider that the condensation with pyruvic acid would proceed in the direction of formation of mainly pyrazinopyridothiazole (D).



(D)

Condensation products with diacetyl* (VI), dibenzyl (VII), phenylglyoxal (IX), pyruvic acid (VIII), acenaphthoquinone (XI) and phenanthrenequinone (X) were prepared by heating the components in an alcoholic solution. The condensation product with the bisulfite derivative of glyoxal (III) was prepared in aqueous solution, while that with oxalic acid (V) was prepared in 15% hydrochloric acid.

The derivatives of 2-aminopyrazino-[5,6-b]-pyrido-[2,3-d]-thiazole, synthesized by us, are shown in the table. They are crystalline compounds, colored light yellow and in their properties resembling compounds with condensed nitrogenous heterocycles, for example derivatives of pyrido-[2,3-b]-pyrazine, pyrimido-[4,5-b]-pyrazine (pteridine) etc. Thus, like amino- and hydroxy derivatives of pyrido-[2,3-b]-pyrazine [6] and pteridine [7], the derivatives of 2-aminopyrazino-[5,6-b]-pyrido-[2,3-d]-thiazole have high melting points and mainly decompose at above 300° without melting. They are also poorly soluble in water and organic solvents.

Albert and co-workers [7] showed that the high melting points and poor solubility in water and organic solvents of the amino and the hydroxy derivatives of pteridine are explained by the presence of intermolecular hydrogen bonds in which atoms of nitrogen and the amino and hydroxy groups participate. Evidently, the same type of intramolecular association exists among the bases synthesized by us.

Derivatives of 2-aminopyrazino-[5,6-b]-pyrido-[2,3-d]-thiazole are stable compounds; on being boiled for a long time with 10% solution of sodium hydroxide, no evolution of ammonia is observed. They form hydrochlorides and sulfates with hydrochloric and sulfuric acids. With picric acid they form picrates which crystallize well from water. Derivatives of 2-aminopyrazinopyridothiazole with hydroxy groups (IV, VIII) dissolved in dilute alkalies and did not dissolve in solutions of carbonates of the alkali metals. The condensation products of 2,5,6-triaminopyrido-[2,3-d]-thiazole with acenaphthenequinone and phenanthrenequinone (XI, X) form intensely colored solutions in concentrated hydrochloric and sulfuric acids like the products of condensation of derivatives of 2,3-diaminopyridine with the same quinones [8]. Derivatives of 2-aminopyrazino-[5,6-b]-pyrido-[2,3-d]-thiazole are difficult to combust and for this reason the analyses for carbon, hydrogen and nitrogen, by Dumas' method, are low. Analysis for sulfur, by Carius' method, gave satisfactory results.

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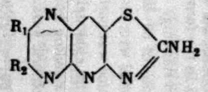
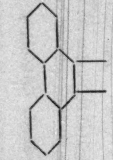
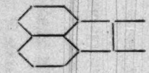
*See table (in parentheses are numbers of the preparations).

Pyrazino-[5,6-b]-Pyrido-[2,3-d]-Thiazoles 

No. of compound	R₁	R₂	Yield (in %)	λ_{max} (m μ)	λ_{min} (m μ)	Empirical formula	Sulfur content (in %)	
							found	calculated
(III)	H	H	73	230, 256, 363	242, 280	$C_8H_5N_5S$	15.64, 15.96	15.76
(IV)	OH	OH	65	225, 255, 280, 350	247, 273, 305	$C_8H_5O_2N_5S$	13.24, 13.54	13.61
(V)	OH	OH	74			$C_8H_5O_2N_5 \cdot HCl$	11.60, 12.01	11.78
(VI)	CH_3	CH_3	81	232, 253, 365, 372	246, 297	$C_{10}H_9N_5S$	14.01, 14.15	13.85
(VII)	C_6H_5	C_6H_5	98	258, 387, 398	325	$C_{20}H_{13}N_5S$	8.78, 8.67	9.01
(VIII)	OH	CH_3	93	246—250, 277, 326, 370	240, 263, 290, 355	$C_9H_7ON_5S$	14.14, 14.04	13.64
(IX)	H	C_6H_5	98	256, 380, 394	310	$C_{14}H_9N_5S \cdot H_2O$	10.93, 10.97	10.77
(X)			99	265, 273, 320, 410, 432	314, 340, 417	$C_{20}H_{11}N_5S \cdot 2H_2O$	8.06, 8.29	8.22
(XI)			99	234, 264, 336, 410	252, 285, 368	$C_{18}H_9N_5S \cdot 2H_2O$	8.42, 8.29	8.81

Since the derivatives of 2-aminopyrazino-[5,6-b]-pyrido-[2,3-d]-thiazole cannot be characterized by melting points, in the tables are shown the maxima and the minima of absorption by their alcoholic solutions in the ultraviolet region. The measurements were made with the SF-4 spectrophotometer.

EXPERIMENTAL

Preparation of 2,5,6-Triaminopyrido-[2,3-d]-Thiazole

2,6-Diamino-3-nitropyridine was prepared by nitration of 2,6-diacetamidopyridine and subsequent hydrolysis of the resulting nitrodiacetamidopyridine [5].

2,5-Diamino-6-nitropyrido-[2,3-d]-thiazole (II). To a solution of 15.4 g of 2,6-diamino-3-nitropyridine in 850 ml of 95% acetic acid we added 38.8 g of potassium thiocyanate; the resulting solution was cooled to − 5° and at this temperature 16 g of bromine was added to it with mechanical stirring slowly and dropwise. After completion of the bromine addition, the mixture was stirred for 15 minutes at 0° and 40 minutes at room temperature, was then heated to 70°, treated with 50 ml of water and the mixture was heated on a steam bath for 15 minutes. The hot solution was filtered from the insoluble orange precipitate of the thiocyano polymer. The filtrate was cooled to 0° and made carefully alkaline with concentrated ammonium hydroxide solution. The resulting yellow precipitate was filtered off, washed with water, alcohol and ether and dried in air. Its weight was 15.4 g (73%). It was recrystallized from hot ethylene glycol or pyridine. Orange yellow plates which decomposed at 315° without melting.

Found %: N 33.18, 32.93; S 15.21, 15.33. $C_6H_5O_2N_5S$. Calculated %: N 33.17; S 15.16.
λ_{max} 284, 318, 420 mμ; λ_{min} 248, 303, 355 mμ.

2,5,6-Triaminopyrido-[2,3-d]-thiazole (I). To a suspension of 10 g of 2,5-diamino-6-nitropyrido-[2,3-d]-thiazole (II) in 150 ml of alcohol we added 10 ml of 20% acetic acid and 30 g of iron shavings; the mixture was refluxed on a water bath with mechanical stirring for one hour. Fifty ml of water was added in small portions during this period. The heating on the water bath and the stirring were continued for one hour longer, after which 4 ml of 40% solution of sodium hydroxide was added and the hot solution was filtered. The precipitate was extracted several times with hot alcohol (70%). A crystalline substance (2.8 g) crystallized in the form of pink needles, which decomposed at 252-253°, from the filtrate which gradually turned dark on standing. The blue-green filtrate was evaporated under vacuum at the water pump on a water bath to a volume of 30-40 ml. Some black crystals crystallized on standing from the residue. These were filtered off and washed with alcohol and ether. The weight of the crystals was 2.1 g for a total yield of 4.9 g (57%). The compound was purified by recrystallization from either 70% alcohol with charcoal or from dilute hydrochloric acid with charcoal. Colorless needles of the dihydrochloride of 2,5,6-triaminopyrido-[2,3-d]-thiazole precipitated on standing from the hydrochloric acid solution. These were recrystallized for analysis once more from 15% hydrochloric acid.

Found %: S 12.36, 12.50; Cl 27.91, 27.80. $C_6H_7N_5S \cdot 2HCl$. Calculated %: S 12.59; Cl 27.95.

The hydrochloride was dissolved in a small volume of water and neutralized with aqueous ammonium hydroxide. The base precipitated in the form of nearly colorless needles. These were recrystallized from alcohol. It formed colorless needles which darkened at 240° and melted with decomposition at 253°.

Found %: N 38.34, 38.14; S 17.52, 17.30. $C_6H_7N_5S$. Calculated %: N 38.67; S 17.68.
λ_{max} 225, 280-5, 341 mμ; λ_{min} 257, 305 mμ.

The sulfate was prepared by mixing the alcoholic solution of the base with an excess of an aqueous solution of sulfuric acid. The resulting colorless crystalline precipitate was recrystallized from water.

Found %: S 22.90, 22.81. $C_6H_9O_4N_5S_2$. Calculated %: S 23.10.

The triacetate of 2,5,6-triaminopyrido-[2,3-d]-thiazole was prepared by a brief heating of the base at reflux with excess acetic anhydride. The resulting colorless precipitate was recrystallized from acetic acid. It did not melt on being heated to 320°.

Found %: S 10.08, 10.13. $C_{12}H_{14}O_3N_5S$. Calculated %: S 10.38.
λ_{max} 228, 275-280, 322 mμ; λ_{min} 293 mμ.

2-Aminopyrazino-[5,6-b]-pyrido-[2,3-d]-thiazole (III). A hot solution of 0.54 g of 2,5,6-triaminopyrido-[2,3-d]-thiazole in 10 ml of water was mixed with a hot solution of 1.15 g of the bisulfite derivative of glyoxal in 85 ml of water and the mixture was heated for two hours on a steam bath. On cooling, the resulting crystalline precipitate, which had a yellow color, was filtered off, washed with water, alcohol and ether, and dried in air. The weight of the precipitate was 0.64 g; it was poorly soluble in water and alcohol, readily soluble in hot ethylene glycol. It was recrystallized from ethylene glycol. For analysis it was recrystallized once more from a large volume of water. Light yellow needles which decomposed above 300° without melting.

2-Amino-6,7-dimethylpyrazino-[5,6-b]-pyrido-[2,3-d]-thiazole (VI). To a hot solution of 0.45 g of 2,5,6-triaminopyrido-[2,3-d]-thiazole in 20 ml of 70% alcohol we added a solution of 0.3 g of diacetyl in 10 ml of alcohol. The mixture was refluxed for one hour on a water bath and the resulting precipitate (0.56 g) was filtered off, washed with alcohol and ether and dried in air. The compound was poorly soluble in water, alcohol and other organic solvents. It was recrystallized from ethylene glycol for purification. It formed light yellow needles which did not melt at 320°. Its alcoholic and aqueous solutions fluoresced in light.

Compounds (VII-XI) in the table were prepared similarly.

2-Amino-5,6-dihydroxypyrazino-[5,6-b]-pyrido-[2,3-d]-thiazole (IV). A mixture of 0.54 g of 2,5,6-triaminopyrido-[2,3-d]-thiazole, 0.5 g of oxalic acid and 20 ml of 15% hydrochloric acid was refluxed for two hours. After 10-15 minutes a colorless crystalline precipitate (0.6 g) began to separate from the solution. It was filtered off, washed with a small volume of cold water, alcohol and ether. The salt was dissolved in 2% solution of sodium hydroxide, the solution was filtered and neutralized with 2% acetic acid solution. The resulting precipitate was filtered off and washed with water and alcohol. This operation was repeated twice. The amorphous light yellow powder did not melt at 300°. Its aqueous and alcoholic solutions fluoresced.

SUMMARY

1. 2,5-Diamino-6-nitropyrido-[2,3-d]-thiazole was prepared by thiocyanation of 2,6-diamino-3-nitropyridine. By the reduction of this compound there was obtained 2,5,6-triaminopyrido-[2,3-d]-thiazole.

2. By condensation of 2,5,6-triaminopyrido-[2,3-d]-thiazole with α-dicarbonyl compounds a series of derivatives of 2-aminopyrazino-[5,6-b]-pyrido-[2,3-d]-thiazole was prepared.

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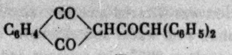
2-DIPHENYLACETYL-1,3-INDANEDIONE

Ia. K. Ozol, V. N. Zelmen and G. Ia. Vanags

Recently there appeared an interest in 2-substituted 1,3-indanediones in connection with the physiological activity shown by them. According to literature data, some of these compounds have antibacterial, others – insecticidal activity. 2-Phenylindanedione is an active blood anticoagulant and is already being used in practice. An even more active blood anticoagulant is 2-diphenylacetyl-1,3-indanedione (I). It differs from the other blood anticoagulants in use, such as dicoumarol or phenylindanedione, by the fact that in even small doses it causes a considerable drop of the prothrombin level of the blood. In addition, it was discovered that diphenylacetylindanedione is a valuble substance for control of rodent pests.



$$C_6H_4\left\langle\begin{matrix}CO\\ CO\end{matrix}\right\rangle CHCOCH(C_6H_5)_2$$

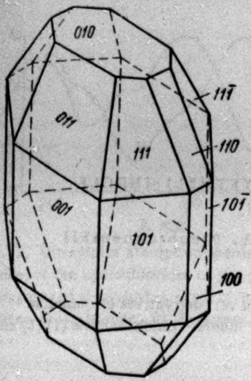
(I)

EXPERIMENTAL

Diphenylacetylindanedione was prepared by condensation of dimethyl- or diethyl-phthalate with diphenylacetone by the general method of Claisen. The best result – yield of 42 % – was obtained in running the condensation in 1:1.3 molar ratio of diphenylacetone and dimethyl phthalate [1]. In its general lines the analogous synthesis has been described in an American patent, which indicated a yield of 37% [2].

Diphenylacetylindanedione is a yellow crystalline substance with m.p. 146-147° (with decomposition). It is soluble in the usual organic solvents, for example alcohol, acetone, chloroform, carbon tetrachloride, benzene, toluene, glacial acetic acid and others; it may be recrystallized from these solutions. Diphenylacetylindanedione at first separates from its solution in acetone in the form of needle-shaped crystals which after standing in acetone are transformed rather rapidly (0.5-1 hour) into large yellow, well-formed prismatic crystals.

Expt. No.	Simple forms	Symbol	ρ	φ	No. of observ.	Accuracy
1	Prism	111	50°30′	43°48′	7	±10′
2	"	$11\bar{1}$	132°36′	50°41′	5	±15′
3	"	011	40°24′	83°57′	6	+15′
4	"	101	41°24′	0°00′	7	±10′
5	"	$10\bar{1}$	145°24′	0°00′	7	±10
6	"	110	90°00′	47°18′	2	±20′
7	Pinacoid	100	90°00′	0°00′	1	±30
8	"	010	90°00′	90°00′	7	±10′
9	"	001	5°13′	0°00′	7	±10′



Crystal of 2-diphenylacetylindanedione.

The density of the crystals of 2-diphenylacetyl-1,3-indanedione was determined pycnometrically by using water as the filling liquid. Since the crystals are somewhat soluble in water, the resulting value of density was not accurate: d_{20} 1.35 ± 0.10 g/cm^3.

Crystals of 2-diphenylacetyl-1,3-indanedione show oblique extinction under polarized light in one of the crystallographic directions, which indicates the relationship of the crystals to monoclinic syngony.

Goniometric data on the crystals are shown in the table.

It follows from the goniometric measurements that crystals of 2-diphenylacetyl-1,3-indanedione belong to the prismatic class of monoclinic syngony (see figure).

The monoclinic angle β = 95°13' ± 10'. The ratio of crystallographic axes: a : b : c = 1.074 : 1 : 0.839.

For the determination of parameters of the elemental cell there were taken the x-ray patterns of rotation of the monocrystals along the crystallographic directions. Copper K_α radiation was used.

a = 13.24 A, b = 12.36 A, c = 10.35 A. X-Ray ratio of axes: a : b : c = 1.071 : 1 : 0.837. Volume of elemental cell V = abc sin β = 1694 A^3.

Four molecules fit the elemental cell.

$$Z=\frac{VdN}{M}=\frac{1694\cdot10^{-24}\cdot1.35\cdot0.602\cdot10^{24}}{340.36}=4.05\approx4.$$

X-ray density d_x = 1.335 g/cm^3.

For the determination of the translational group we took the x-ray patterns of rotation along directions [110] and [011]. The x-ray diffraction patterns showed that the structure has a primitive elemental Brevet cell.

For the determination of the space group of symmetry, we took the Weisenbergograms in the directions [010] and [100]. Among the existing reflections there was found the following regularity: hkl – no limits, hol – present with h = 2n, oko – present with k = 2n.

This regularity of extinctions singularly determines the space group at $C_{2h}^5 - P^{21}/c$.

SUMMARY

1. By condensation of dimethyl phthalate with diphenylacetone there was prepared 2-diphenylacetyl-1,3-indanedione which, according to the literature data, is a strong blood anticoagulant. Diphenylacetylindanedione crystallized well from acetone in the form of large pale yellow, well-formed crystals (0.1-1.5 mm) with m.p. 146-147°.

2. Crystals of 2-diphenylacetyl-1,3-indanedione belong to the prismatic class of monoclinic syngony: a = 10.35 A, b = 12.36 A, c = 13.24 A, β = 95°13'. The lattice constants were determined by x-ray diffraction patterns with rotation of the crystals under copper K_α-radiation. V = 1694 A^3; Z = 4. The space group: $C_{2h}^5 - P^{12}/c$.

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SYNTHESIS OF 2-(α-PYRIDYL)-3(β-HYDROXYETHYL)-INDOLE

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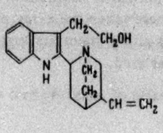
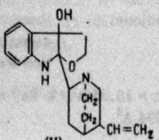
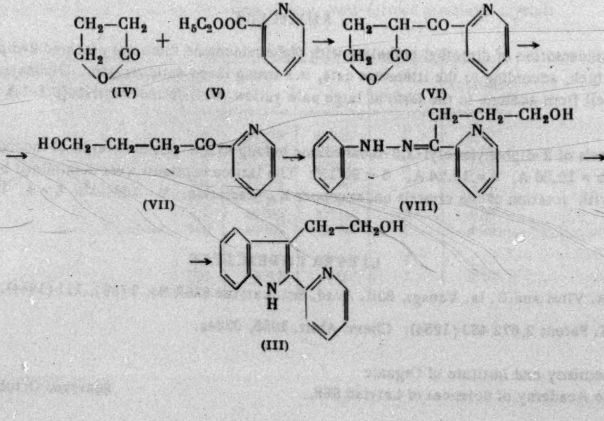
The alkaloids of the quinine bark are subdivided into two large groups of: derivatives of quinoline – quinine, quinidine, cinchonine, cinchonidine and others, and derivatives of indole – cinchonamine (I) [1] and quinamine (II) [2].


(I)


(II)

Syntheses of the fundamental alkaloids of the quinoline group, including quinine itself, have been realized at the present time [3]. Quinine alkaloids of the indole structure have not been studied sufficiently in the synthetic aspect, although they represent a considerable area of interest owing to their biogenetic and structural relationship with such valuable compounds, in the physiological sense, as reserpine (serpasil), yohimbine etc.

We made some studies directed to the development of the paths of synthesis of the most important quinine alkaloid of the indole group – cinchonamine. In the present paper is described the preparation of the analog of cinchonamine, 2-(α-pyridyl)-3-(β-hydroxyethyl)-indole (III) by the reaction scheme which opens the way to the synthesis of cinchonamine itself.



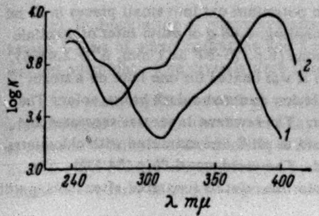


Fig. 1. Ultraviolet absorption spectra in alcohol of the hydrochlorides of phenylhydrazones of α-pyridyl-ω-hydroxypropyl ketone. 1) α-Isomer, 2) β-isomer.

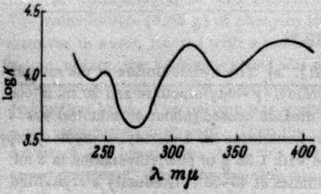
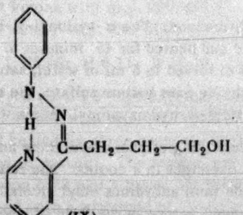


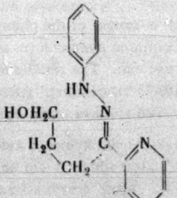
Fig. 2. Ultraviolet absorption spectrum in alcohol of the base of 2-(α-pyridyl)-3-(β'-hydroxyethyl)-indole.

Condensation of γ-butyrolactone (IV) with ethyl ester of picolinic acid (V) led to α-pyridoyl-γ-butyrolactone (VI), which on being heated with hydrochloric acid was transformed into α-pyridyl-ω-hydroxypropyl ketone (VII). The phenylhydrazone of this ketone (VIII) was obtained in two forms of isomers which differed in physicochemical properties. They were separated by the chromatographic route. The base of the α-isomer was eluted much more readily than was the base of the β-isomer. Ultraviolet absorption spectra of the isomeric phenylhydrazones in ethyl alcohol were similar to each other but the absorption maxima for α-isomer were shifted toward the shorter wavelengths in comparison with those of the β-isomer (Fig. 1).

The β-isomer of the phenylhydrazone has a more basic character in comparison with the α-isomer. Thus, in the presence of an insufficient amount of hydrogen chloride the β-isomer reacts first. The lesser basicity of the α-isomer may be explained by the fact that hydrogen at a secondary nitrogen and nitrogen in the pyridine ring are closely disposed relative to each other and between them the formation of a hydrogen bond is possible. The β-isomer of the phenylhydrazone readily loses one mole of water on being heated in vacuum, which is not observed for the α-isomer. This occurs, evidently, because in the β-isomer the hydroxyl group and the hydrogen at the secondary nitrogen atom are close to each other and can be readily cleaved in the form of water with formation of a compound with a six-membered ring (XI). In accordance with this, the α-isomer must be assigned the syn-configuration (IX), while the β-isomer should have the anti-configuration (X) relative to the α-pyridyl group.



(IX)



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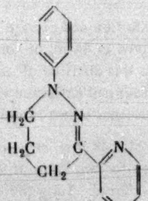

(XI)

The α-isomer of phenylhydrazone of α-pyridyl-ω-hydroxypropyl ketone could not be transformed into an indole derivative despite many attempts to run the reaction in the presence of various catalysts (hydrochloric acid, sulfuric acid, hydrogen chloride, boron trifluoride in acetic acid, boron trifluoride etherate). On heating the hydrochloride of the phenylhydrazone of α-pyridyl-ω-hydroxypropyl ketone (β-isomer) with concentrated hydrochloric acid we isolated 2-(α-pyridyl)-3-(β'-hydroxyethyl)-indole (III) from the reaction mixture. The ultraviolet absorption spectrum of base (III) (Fig. 2) indicates the presence of the indole ring conjugated with the pyridine ring.

An analogous scheme, based on the condensation of γ-butyrolactone with the ethyl ester of 3-vinylquinuclidine-6-carboxylic acid, permitted us to accomplish the synthesis of the alkaloid cinchonamine.

EXPERIMENTAL

1. α-(2-Pyridoyl)-γ-butyrolactone (VI). To 2.5 g of metallic potassium cut into small pieces in 25 ml of dry benzene we added, over 10 minutes with stirring and external cooling, 9.66 g of ethyl ester of picolinic acid (b.p. 110-112° at 7 mm, $n^{20}D$ 1.5096) and 5.5 g of γ-butyrolactone (b.p. 75-80° at 7 mm, $n^{20}D$ 1.4356). The reaction mixture was set aside for one hour at 20-30° after which it was heated for one hour on a steam bath. Potassium gradually disappeared during the reaction and the solution assumed a dark brown color. The mixture was left overnight. Then to it was added 13 ml of cold water. The benzene layer was separated and washed with water. The aqueous layer was neutralized with acetic acid to pH 7 and extracted with chloroform. After drying, the solvent was distilled off and the residue was distilled. The yield was 6.65 g (54.3%). The substance was isolated in the form of a light yellow oil from which colorless crystals separated after rubbing with ether. B.p. 144-149° (0.3 mm), m.p. 46.5-47.5°.

Found %: C 62.60, 62.82; H 4.51, 4.57; N 7.49, 7.41. $C_{10}H_9O_3N$. Calculated %: C 62.82; H 4.74; N 7.32.

Reineckate of α-(2-pyridoyl)-γ-butyrolactone was prepared by the reaction of α-(2-pyridoyl)-γ-butyrolactone in alcohol with the Reinecke salt after being heated on a water bath for several minutes. The resulting precipitate was recrystallized from water. There were obtained crystals, colored slightly pink, with m.p. 156-159°.

Found %: N 19.56, 19.24. $C_{14}H_{16}O_3N_7S_4Cr$. Calculated %: N 19.21.

2. Phenylhydrazones of α-pyridyl-ω-hydroxypropyl ketone (VIII). a) The hydrochloride of the mixture of α- and β-isomers of the phenylhydrazones. Heating 2.8 g of α-pyridoyl-γ-butyrolactone and 20 ml of concentrated hydrochloric acid at 120-130° until the evolution of carbon dioxide ceased (about 40 minutes) was followed by distillation of the solvent in vacuum at 40°. The crude hydrochloride of α-pyridyl-ω-hydroxypropyl ketone was dissolved in 5 ml of anhydrous methyl alcohol and treated with 1.58 g of phenylhydrazine in 3 ml of methyl alcohol. The mixture was heated on a water bath for 35 minutes at 40-50°. Gradually a crystalline yellow precipitate formed. The precipitate was filtered off on the following day and washed with alcohol and ether. Yield: 3.87 g (98 %). M.p. 126-132°. After four recrystallizations from anhydrous alcohol there was obtained the hydrochloride which represents the mixture of two isomers; m.p. 167.5-168°.

Found %: C 61.94, 61.60; H 6.11, 6.38; N 14.30, 14.33. $C_{15}H_{18}ON_3Cl$. Calculated %: C 61.75; H 6.21; N 14.40.

b) Hydrochloride and picrate of α-isomer of the phenylhydrazone. The α-pyridoyl-γ-butyrolactone (4.7 g) was dissolved in 34 ml of concentrated hydrochloric acid and heated for 45 minutes to 120-130°. The hydrochloric acid was distilled off in vacuum. The residue was dissolved in 5 ml of water, saturated with potassium carbonate and extracted with 75 ml of ether. After drying over sodium sulfate, the ether was distilled. There remained a light brown liquid. The yield of crude α-pyridyl-ω-hydroxypropyl ketone was 3.86 g (95%).

A mixture of 1.48 g of α-pyridyl-ω-hydroxypropyl ketone, 0.78 g of phenylhydrazine and 3 ml of absolute ether was set aside for two hours at 25°, after which it was kept overnight in a cooler. The resulting crystals were filtered off. Yield: 1.4 g (89.6%). After recrystallization from anhydrous ethyl alcohol there was obtained the α-isomer of the phenylhydrazone of α-pyridyl-ω-hydroxypropyl ketone in the form of needle-shaped crystals with yellow color. Yield: 0.49 g (36.7%); m.p. 96-97°.

Found %: N 16.37, 16.25. $C_{15}H_{17}ON_3$. Calculated %: N 16.46.

Hydrochloride of α-isomer of phenylhydrazone of α-pyridyl-ω-hydroxypropyl ketone was isolated in the form of yellow crystals, readily soluble in water, and less soluble in alcohol and acetone, and insoluble in ether and benzene. M.p. 187-188°.

Found %: C 61.87, 61.75; H 6.27, 6.30; N 14.56, 14.50. $C_{15}H_{18}ON_3Cl$. Calculated %: C 61.75; H 6.21; N 14.40.

Picrate of α-isomer of phenylhydrazone of α-pyridyl-ω-hydroxypropyl ketone – brick red crystals (from anhydrous ethyl alcohol). M.p. 149-149.5°.

Found %: C 51.90, 52.18; H 4.05, 4.13; N 17.55, 17.48. $C_{21}H_{20}O_8N_6$. Calculated %: C 52.06; H 4.16; N 17.36.

c) Hydrochloride of phenylhydrazone of β-isomer. A mixture of 0.86 g of α-pyridyl-ω-hydroxypropyl ketone, 0.57 g of phenylhydrazine and 2 ml of absolute ether was heated at 80° for 50 minutes, after which it was left overnight. The crystals were filtered off. Yield: 1.3 g (97%); m.p. 52-56°.

The phenylhydrazone (0.2 g) was left overnight in a desiccator containing a few drops of ether saturated with hydrogen chloride. On the next day the precipitate was treated with dry benzene. There remained 0.09 g of benzene-insoluble hydrochloride of phenylhydrazone with m.p. 256-257°. After recrystallization from anhydrous ethyl alcohol we isolated the hydrochloride of β-isomer of phenylhydrazone of α-pyridyl-ω-hydroxypropyl ketone in the form of yellow crystals; m.p. 257-257.5° (with decomposition).

Found %: C 61.75, 62.08; H 6.40, 6.11; N 14.20, 14.28. $C_{15}H_{18}ON_3Cl$. Calculated %: C 61.75; H 6.21; N 14.40.

From the benzene solution we obtained 0.1 g of a base with m.p. 67-75°, which was changed to the hydrochloride. After recrystallization from anhydrous ethyl alcohol we isolated 0.03 g of the hydrochloride of α-isomer of phenylhydrazone of α-pyridyl-ω-hydroxypropyl ketone with m.p. 187-188°.

3. Chromatographic separation of isomeric phenylhydrazones of α-pyridyl-ω-hydroxypropyl ketones. The hydrochloride (0.65 g) of phenylhydrazone of α-pyridyl-ω-hydroxypropyl ketone (from experiment a) was dissolved in water, treated with a sodium hydroxide solution and extracted with benzene. After drying with sodium sulfate, the benzene extract was passed through a column (20 cm in height and 1.1 cm diameter) filled with aluminum oxide. The phenylhydrazone base adsorbed in the upper zone of the column with formation of a dark yellow band. The column was washed first with 20 ml of a mixture of ethyl alcohol and benzene (1:1). A red band passed downward. Then the column was washed with ethyl alcohol, whereupon a yellow band passed downward at a lower rate. After this, the column was washed with methyl alcohol, and another yellow band passed downward. From the benzene-alcohol fraction, after distillation of the solvents, there was isolated 0.16 g of red amorphous substance which was transformed into the hydrochloride. After recrystallization from anhydrous ethyl alcohol we isolated 0.07 g of α-isomer of the phenylhydrazone. This substance, after being dried at 100° at 2 mm, was unchanged and had m.p. 187-188°.

From the alcohol fraction, after distillation of the solvent, we obtained 0.076 g of a hygroscopic red amorphous substance from which was isolated 0.014 g of hydrochloride of β-isomer of phenylhydrazone of α-pyridyl-ω-hydroxypropyl ketone with m.p. 257-257.5°. The substance after being dried for one hour at 110° and 2 mm lost one mole of water. M.p. 257-258°.

Found %: C 65.49; H 6.11; N 15.29. $C_{15}H_{16}N_3Cl$. Calculated %: C 65.79; H 5.88; N 15.34.

4. 2-(α-Pyridyl)-3-(β'-hydroxyethyl)-indole (III). The hydrochloride of phenylhydrazone of α-pyridyl-ω-hydroxypropyl ketone with m.p. 257-259° (0.3 g; β-isomer) was dissolved in 8 ml of concentrated hydrochloric acid and heated for three hours at 120-130°. The reaction mixture assumed a brown color. Hydrochloric acid was distilled in vacuum. The residue was dissolved in 4 ml of water, made alkaline with sodium hydroxide solution, whereupon 0.23 g of a brown precipitate formed, which was recrystallized from dry acetone. The substance crystallized with a molecule of the solvent. M.p. 107-110° (changes at 80°).

Found %: N 9.44. $C_{15}H_{14}ON_2 \cdot C_3H_6O$. Calculated %: N 9.45.

Picrate of 2-(α-pyridyl)-3-(β'-hydroxyethyl)-indole was obtained by treatment of an alcoholic solution of the base with an alcoholic solution of picric acid. After two recrystallizations from alcohol we obtained the picrate of 2-(α-pyridyl)-3-(β'-hydroxyethyl)-indole in the form of yellow crystals. M.p. 238.5-239.5°.

Found %: C 53.70, 54.20; H 3.81, 3.63; N 14.63, 14.85. $C_{21}H_{17}O_8N_5$. Calculated %: C 53.95; H 3.66; N 14.98.

SUMMARY

The scheme of a synthesis of 2-(α-pyridyl)-3-(β-hydroxyethyl)-indole was developed which permits the realization of synthesis of the alkaloid cinchonamine.

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Moscow Institute of Fine Chemical Technology Received September 13, 1957

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* In Russian.

COMPARATIVE STUDY OF CHEMICAL STRUCTURE OF SKB RUBBER AND SKBM RUBBER BY THE METHOD OF OZONOLYSIS

A. I. Iakubchik, A. I. Spasskova, A. G. Zak and I. E. Shostatskaia

The properties of butadiene rubbers are closely related to the conditions of running the polymerization process and the nature of the initiator used. In USSR there are being manufactured three kinds of butadiene rubbers prepared in the presence of alkali metals: sodium-butadiene rubber (SKB), potassium-butadiene (SKV) and lithium-butadiene (SKBM) rubbers. The significant difference between them consists of the fact that rubber SKBM has a lower glazing temperature than rubber SKB and has higher elastic properties. Rubber SKV in its properties occupies an intermediate position between SKB and SKBM [1]. The glazing temperature and the elasticity of butadiene rubbers are determined by the ratio of 1,4- and 1,2-links in them. Butadiene rubbers having frost-resistance are characterized by a lowered percentage of the 1,2-links [2]. The chemical structure of butadiene rubbers is determined not only by the percentage of the 1,4- and the 1,2-links but also by the mutual disposition of these links in the polymer and is but one of the factors which determine the properties of the rubbers. In the study of structure of various butadiene rubbers there were established the areas formed by combination of butadiene molecules in the positions : -1,4-1,4-, -1,4-1,2-1,4-, -1,4-(-1,2-)$_2$-1,4-, and -1,4-1,4- with branching at the α-methylene group [3-5]. The magnitude of these areas depends on the conditions of formation of the polymers.

We ran a comparative study of the chemical structure of rubbers SKB and SKBM differing from each other in frost-resistance. The chemical structure of the rubbers was studied by ozonolysis method. For separation of the acids, obtained after oxidative decomposition of the ozonides, we used the method of partition chromatography. Chromatograms of acidic products of ozonolysis of the rubbers under investigation were obtained. On the basis of these chromatograms and the chemical characterization of some of the acids in the ozonolysis products, the following acids were established: succinic, butane-1,2,4-tricarboxylic, propane-1,2,3-tricarboxylic, hexane-1,x,y,6-tetracarboxylic, formic and levulinic[*] whih were found also in the products of ozonolysis of other butadiene rubbers [3-5]. On Figures 1-4 are shown the chromatograms of acids isolated from ozonolysis products of the rubbers being studied. On the chromatograms there is calculated the percentage of the hydrocarbon skeleton of the rubbers in the areas of the different structures. The results are collected in Table 1.

In the products of oxidative decomposition of the ozonides there was 77% of the carbon skeleton of rubber SKB and 82.6% of carbon skeleton of rubber SKBM. In areas of known structure there was 47.1% of the carbon skeleton of SKB rubber and 54.6% of the carbon skeleton of SKBM rubber. The unaccounted-for carbon skeleton of the rubbers was contained in acids whose structure was not determined and to which the peaks: I, V, X and XI (in Fig. 1, chromatogram 1) and I, IV and IX (Fig. 2, chromatogram 1), correspond in the chromatograms as well as in formic acid, which distilled with the solvent from the products of oxidative decomposition of the ozonides, in neutral and gaseous products which were not studied by us and in acetic acid. Acetic acid may form in isomerization of the areas with external double bonds [5] and in decomposition of levulinic acid in acid medium. Acetic acid was not taken into account by us since the oxidative decomposition of the ozonides was run in the medium of glacial acetic acid. In rubber SKBM the same structure of the units was found as in SKB.

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[*] Levulinic acid was found only in the products of ozonolysis of rubber SKB. In ozonolysis products there may exist three isomeric hexanetetracarboxylic acids: hexane-1,2,4,6-, hexane-1,3,5,6-, and hexane-1,2,5,6-tetracarboxylic acids formed respectively from areas of: -1,4-(1,2-)$_2$-1,4-, -1,4-1,2-2,1-1,4-, and -1,4-2,1-1,2-1,4-.

TABLE 1

Name	Structure of area of polymer from which the acid formed	% hydrocarbon skeleton of the rubber in these areas		% of additions of butadiene in positions 1,4 and 1,2 in the rubber			
		SKB	SKBM	SKB		SKBM	
				1,4	1,2	1,4	1,2
Levulinic	—1,4—1,2—1,4—	7.6	—	3.8	3.8	—	—
Succinic	—1,4—1,4—	11.1	24.0	11.1	—	24.0	—
Butane-1,2,4-tricarboxylic	—1,4—1,2—1,4—	14.8	22.0	7.4	7.4	11.0	11.0
Propane-1,2,3-tricarboxylic	—1,4—1,4— with branching at α-methylene group * *	7.5	4.7	7.5	—	4.7	—
Hexane-1,x,y,6-tetracarboxylic	—1,4—(—1,2—)—1,4—	6.1	3.9	2.0	4.1	1.3	2.6
Total		47.1	54.6	31.8	15.3	41.9	13.6

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* In addition, propane-1,2,3-tricarboxylic acid may form from areas 1,4-1,2-1,4- as the abnormal product of ozonolysis [5].

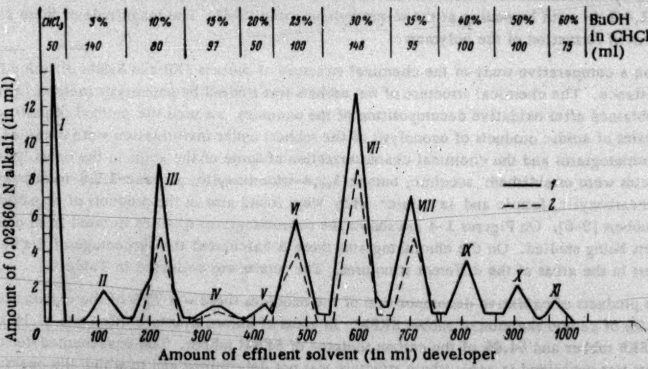

Fig. 1. Chromatogram of separation of viscous acids from products of ozonolysis of rubber SKB (1) and mixture of acids (2).
III – Acetic, IV – formic, VI – succinic, VII – butane-1,2,4-tricarboxylic, VIII – propane-1,2,3-tricarboxylic acids.

It is evident from the data in Table 1 that the percentage of carbon skeleton of the rubber in areas of -1,4-1,4- and -1,4-1,2-1,4- in rubber SKBM is greater than in rubber SKB. The structure of SKBM rubber is more regular and approaches closer to linear. Evidently this is one of the factors which determine frost-resistance. The glazing temperature of rubber SKB was found to be −51.5°, that of rubber SKBM −72.2° [2].

EXPERIMENTAL

Butadiene rubbers SKB and SKBM were obtained by polymerization of butadiene by the technique of rodless polymerization. The rubbers were freed of antioxidant and low-molecular weight fractions by dissolution in benzene with a subsequent double reprecipitation from 1% benzene solution with ethyl alcohol. After this, the rubbers were dried under 2 mm vacuum to a constant weight. The purification, drying and storage of the rubbers were done in the atmosphere of pure nitrogen [6].

In rubber SKB we found %: C 84.45, 84.29; H 11.06, 11.21.

In rubber SKBM we found %: C 87.17, 87.16; H 11.37, 11.11. $(C_4H_6)_x$. Calculated %: C 88.89, H 11.11.

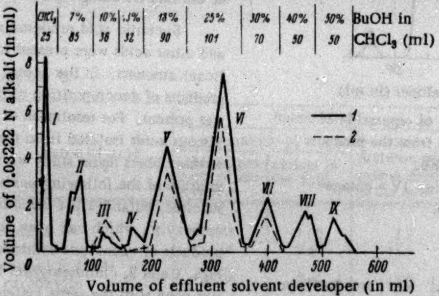

Fig. 2. Chromatogram of separation of viscous acids from products of ozonolysis of rubber SKBM (1) and mixture of acids (2). II – Acetic, III – formic, V – succinic, VI – butane-1,2,4-tricarboxylic, VII – propane-1,2-3-tricarboxylic acids.

Ozonization of the rubbers was run in ethyl acetate at −25° with ozonized oxygen. The ozone concentration in oxygen passing from the ozonizer was 5%. Twenty five g of the rubber was ozonized, for SKB rubber, and 9.8 g of SKBM rubber. In each experiment about 2-2.5 g of rubber was ozonized. There were obtained ozonides which were soluble in ethyl acetate. The solvent was distilled from the ozonide by blowing with dry air at 14-10 mm and 20°. Decomposition of the ozonides was done with acetyl hydroperoxide in a solution of glacial acetic acid with cooling to 0° [7]. Acetyl hydroperoxide was added to the ozonide solution gradually, with the ratio of 1 atom of active oxygen per 1 double bond in the rubber taken for the ozonization; after one day we added a double volume of the hydroperoxide and the mixture was left for several days until a complete decomposition of the ozonides occurred. Excess acetyl hydroperoxide was destroyed by platinum black. Acetic acid was distilled from the products of oxidative decomposition of the ozonides at 4 mm at 30° (water bath temperature) to a constant weight of the residual acids. The products of decomposition of the ozonides had the form of a mixture of viscous and crystalline substances. The crystalline acids were separated from the viscous ones by dissolution of the latter in diethyl ether. After removal of the diethyl ether we obtained 37.7 g of viscous and 3.7 g of crystalline acids from ozonization of rubber SKB and 11.7 g of viscous and 4.1 g of crystalline acids from ozonization of rubber SKBM. In the resulting acids we found 16.4 g of carbon or 77% of carbon skeleton of rubber SKB and 7.0 g of carbon or 82.6% of carbon skeleton of rubber SKBM. The melting point of the crystalline acids, isolated from the products of ozonolysis of the rubbers under study, was 183° after recrystallization from hot water. Mixed melting point with succinic acid (m.p. 183°) was also 183°. Separation of the acids was done chromatographically on silica gel of mark MSK (fine silica gel, roughly porous), as described previously [4, 8]. For separation of the acid mixture of the products of ozonolysis of rubber SKB we used a medium column of 400 mm in height and inner diameter of 18 mm into which was placed 25 g of the silica gel (100-150 mesh) preliminarily rubbed-up with 25 ml of water. For separation of the acid mixture from rubber SKBM we used the small column (height 300 mm, inner diameter 12 mm) into which was placed 12 g of the

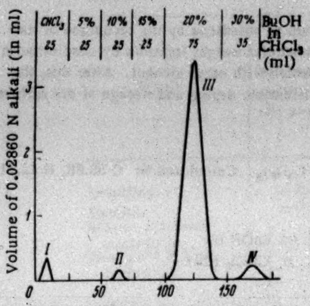

Fig. 3. Chromatogram of separation of crystalline acids isolated from the products of ozonolysis of rubber SKB.
II – Acetic, III – succinic, IV – butane-1,2,4-tricarboxylic acids.

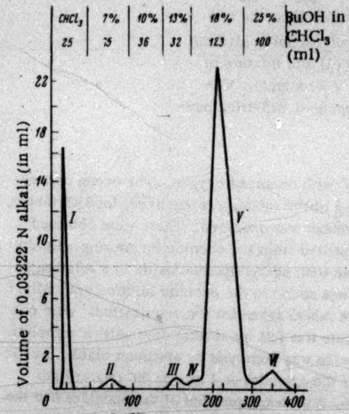

Fig. 4. Chromatogram of separation of crystalline acids isolated from the products of ozonolysis of rubber SKBM.
II – Acetic, III – formic, V – succinic, VI – butane-1,2,4-tricarboxylic.

silica gel. By gradual selection of polarities of the mobile solvent for each mixture of the acids, there was developed a system under which the acid mixtures under investigation were separated sufficiently clearly.

The chromatograms of separation of the viscous acids of the ozonolysis products of rubbers SKB and SKBM are shown on Figures 1 and 2.

Under the same conditions we ran the separation of crystalline acids (Figs. 3 and 4) and acetic acid distilled from the products of decomposition of the ozonides of the rubbers being studied.

Succinic acid predominated in the crystalline acids, and other acids were present in them in only very insignificant amounts. In the acetic acid, distilled from the products of decomposition of the ozonides, no other acid was present. For resolution of the chromatogram of the viscous acids isolated from the products of ozonolysis of the rubbers under study we took chromatograms of a mixture of the following acids: levulinic, acetic, formic, succinic, butane-1,2,4-tricarboxylic, propane-1,2,3-tricarboxylic, which had been previously established in the products of ozonolysis of butadiene rubbers [3-5] (see Figs. 1 and 2, chromatogram 2). Separation of the acids was done with the same system of development and with the same columns. The acids were identified by the volume peaks and by the thresholds of elution [9, 10]. In superposition of the chromatograms of the acid mixture and of the mixed acids under study it is evident that the elution thresholds of the acids coincide and the order in which the acids pass from the column is always preserved. The peaks of the volumes of the acids at times do not coincide somewhat which might be the result of insufficient preservation of identical conditions during the taking of the chromatograms, as for example by the difference in the rate of passage of the mobile solvent.

It follows from Fig. 1 that on the chromatogram of the mixture of acids being studied – products of oxidative decomposition of ozonide of rubber SKB, peak II corresponds to levulinic, peak III – to acetic, peak IV – to formic, peak VI – to succinic, peak VII – to butane-1,2,4-tricarboxylic, peak VIII – to propane-1,2,3-tricarboxylic, peak IX – to hexane-1,x,y,6-tricarboxylic acids.* In peaks I, V, X and XI the nature of the acids was not established.

It follows from Fig. 2 that in the chromatogram of the mixture of acids from the products of oxidative decomposition of the ozonide of rubber SKBM peak II corresponds to acetic acid, peak III – to formic, peak V – to

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* In chromatographic separation of the products of ozonolysis of sodium-butadiene rubber it was established that the acid which passes in the elution of the column with 5% butanol is levulinic acid, and with 40% butanol – hexane-1,x,y,6-tetracarboxylic acid [4, 8].

TABLE 2

Name of acid	Melting point		Neutralization equivalent		Silver content in the salt (%)	
	found	literature data	found	calculated	found	calculated
Succinic	183°	182.8° [11]	59.2	59.0	65.2	65.0
Butane-1,2,4-tricarboxylic	116—117	116—120 [12]	62.9	63.3	—	—
Propane-1,2,3-tricarboxylic	157—158	157—158 [5], 160—161 [13]	58.0	58.6	64.8	65.2

TABLE 3

Name of acid	Rubber SKB		
	amount (in g)		% carbon skeleton of rubber found in the acid
	acids in products of ozonolysis	carbon in the acid	
Levulinic	1.95	1.00	4.7
Succinic	6.01	2.44	11.1
Butane-1,2,4-tricarboxylic	6.36	2.65	13.0
Propane-1,2,3-tricarboxylic	3.88	1.59	7.5
Hexane-1,x,y,6-tetracarboxylic	2.38	1.09	5.1

TABLE 4

Name of acid	Rubber SKBM		
	amount (in g)		% carbon skeleton of rubber found in the acid
	acids in ozonolysis products	carbon in the acid	
Succinic	5.00	2.04	24.0
Butane-1,2,4-tricarboxylic	3.73	1.65	19.3
Propane-1,2,3-tricarboxylic	1.02	0.40	4.7
Hexane-1,x,y,6-tetracarboxylic	0.61	0.28	3.3

succinic, peak VI – to butane-1,2,4-tricarboxylic, peak VII – to propane-1,2,3-tricarboxylic, peak VIII – to hexane-1,x,y,6-tetracarboxylic acids. Peaks I, IV and IX were not identified.

Chromatographic characterization of the acids was confirmed by the data of chemical analysis. For this we collected the peaks which corresponded to succinic, butane-1,2,4-tricarboxylic and propane-1,2,3-tricarboxylic acids. Butyl alcohol and chloroform were distilled from the isolated acids at 1 mm and 30°. The acids, represented by crystalline substances, were washed free of the residual butanol with diethyl ether, dried in a vacuum desiccator and characterized. The data on the chemical characterization of the acids are shown in Table 2.

From the chromatograms of separation of the viscous and the crystalline acids we calculated the amounts of each acid in the products of oxidative decomposition of ozonides of the rubbers being studied and the percentage of the carbon skeleton of the rubbers as found in the acids. The results are shown in Tables 3 and 4.

The amount of external double bonds was calculated on the basis of the quantitative determination of formic acid in the ozonolysis products, and that of formaldehyde [14]. In rubber SKB there was found 49%, in rubber SKBM 38%, of links with external double bonds. The total unsaturation of rubber SKB was determined by the reaction with iodine bromide [15] and was found equal to 86.7%. The unsaturation of rubber SKBM was not determined since it was totally insoluble.

SUMMARY

1. In rubber SKBM we found areas of the same structure as in rubber SKB, but in rubber SKBM the percentage of the carbon skeleton of the rubber in areas of -1,4-1,4- and -1,4-1,2-1,4- is greater than in rubber SKB.

2. The structure of SKBM rubber is more regular. Evidently, the regularity of its structure is one of the factors which determine its frost-resistance.

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CATALYTIC IONIC TELOMERIZATION

II. THE COMPOSITION OF THE FRACTION OF TERPENE CHLORIDES IN THE PRODUCT OF TELOMERIZATION OF ISOPRENE WITH ITS HYDROCHLORIDES.

LINALYL CHLORIDE

K. V. Leets

Prior to the author's work [1, 2] terpene chlorides were synthesized exclusively from the corresponding terpenic alcohols [3-9] or hydrocarbons [10]. The physical constants reported by different authors for terpenic alcohols of a given structure were often inconsistent. It would therefore, appear that the alleged terpenic alcohols were not pure substances but mixtures of various isomers. Especially contradictory were the data for the constants of compounds to which the structure of geranyl chloride and linalyl chloride had been attributed. Conditions for the synthesis of reputedly pure geranyl and linalyl chlorides from linalool were published recently [7, 11]. Raman spectra were employed in those studies to evaluate the purity of the products and to identify them.

The literature has hitherto been lacking in reliable methods of chemical analytis that might have assisted the evaluation of the purity of the prepared terpenic chlorides. We carried out the synthesis of a number of terpenic chlorides by telomerization of isoprene with hydrochlorides of dienic hydrocarbons [1, 2] and we worked out a method of chemical determination of the primary allylic chlorides in the mixtures [12]. In this way the problem of isolation of the various isomers and of determination of their purity was greatly simplified.

In the present work we made a closer study of the composition of the fraction of monoterpenic chlorides (C_{10}) obtained by telomerization of isoprene with its hydrochlorides in presence of stannic chloride as catalyst [1, 2]. We made use of chemical, physicochemical and physical methods of analysis. We also examined the possibility of isolating pure chemical substances from this fraction.

It was previously established [2] that the main components of the fraction under investigation are geranyl chloride and α-terpinyl chloride.

The investigation was facilitated by isolation of the geranyl chloride from the mixture in the form of its compound with hexamethylenetetramine [2]; in order to avoid cleavage of the elements of hydrogen chloride by the action of hexamethylenetetramine, the reaction was conducted at temperatures not higher than 25°,* using a quantity of hexamethylenetetramine not more than 5% larger than the quantity of geranyl chloride contained in the mixture. The resulting mixture of the remaining isomeric terpenic chlorides was subjected to careful fractionation in vacuo in an efficient column. Small fractions were collected. Each fraction was analyzed for refractive index, density, chlorine content, number of double bonds, and geranyl chloride content. Results are represented in Figure 1. Examination of the curves indicates the presence of four main fractions which differ in properties: 1st fraction (5%), containing a mixture of terpenes and traces of terpenic chlorides; 2nd fraction (36%), aliphatic terpenic chlorides free of geranyl chloride; 3rd fraction, cyclic terpenic chlorides (38%) containing 6% of geranyl chloride; 4th fraction aliphatic terpene dihydrochlorides (20%).

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*At higher temperatures hydrogen chloride is split off from the isomeric terpenic chlorides.

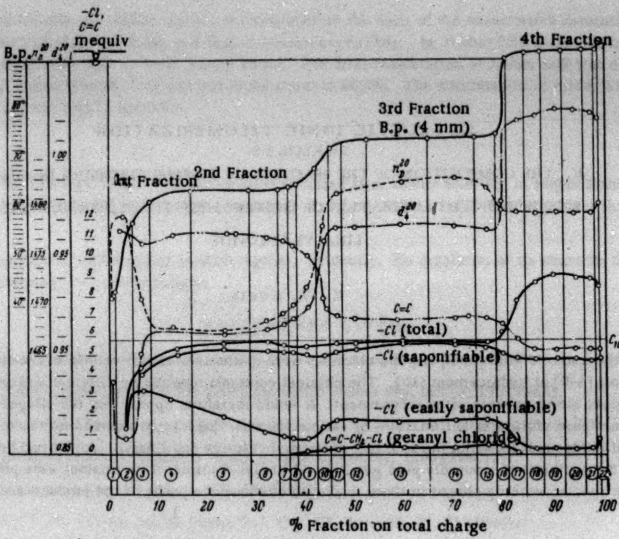

Fig. 1. Rectification of residual terpenic chlorides.

The kinetics of saponification of the 2nd fraction was studied in aqueous acetone solution (using $NaHCO_3$ and also $PbCO_3$ in presence of $Pb(NO_3)_2$), and the kinetic data clearly demonstrated the heterogeneity of the fraction (Fig. 2). Nearly half of the chloride enters into the saponification reaction in the course of 30 minutes, but more than 10 hours is needed for saponification of the whole of the chloride. It was subsequently established that when saponification is conducted at room temperature in an emulsion with aqueous $NaHCO_3$ solution, the reaction is substantially completed in 24 hours, and 45% of the total chloride enters into reaction (Fig. 2). This observation was the basis of development of a method of determination of the easily saponifiable chlorine in terpenic chlorides (see Experimental). The total saponifiable chlorine was determined by the previously described method of saponification of the chloride with boiling aqueous alcoholic solution of $Pb(NO_3)_2$ [1]. Corresponding analyses of the adjacent fractions are presented in Figure 2.

We see from Figure 2 that in the 2nd fraction of aliphatic chlorides the easily saponifiable chlorine is concentrated in the lower-boiling portion, and the difficultly saponifiable chlorine in the higher-boiling portion.

This fraction was subjected to fractional saponification with the objective of identification of the individual components. After the resulting alcohols had been bound in the form of borates with the help of butyl borate [13], a difficultly saponifiable aliphatic terpenic chloride (50% of the total) was separated out by distillation. The kinetics of its saponification was studied. It was also redistilled without undergoing any change in properties. The kinetic behavior and the behavior on redistillation indicated that the substance was pure. Saponification of this chloride gave a primary aliphatic terpenic alcohol with the constants of lavandulol, so that the structure of lavandulyl chloride can be assigned to it (see table, Compound II). The presence in the product of telomerization of a nonallylic aliphatic chloride (lavandulyl chloride) indicates that isoprene hydrochlorides in part (8-10%) add on to isoprene contrary to the Markovnikov rule.

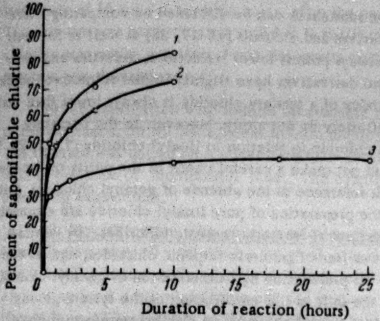

Fig. 2. Kinetics of saponification of the 2nd fraction of low-boiling terpenic chlorides.
1) Saponification with lead carbonate in presence of aqueous acetone solution of lead nitrate at 60°; 2) saponification with sodium bicarbonate in aqueous acetone solution at 60°; 3) saponification with aqueous solution of sodium bicarbonate in emulsion at 20°.

The alcohols isolated from the boric esters were a mixture of geraniol and linalool. We can therefore conclude that the easily saponifiable fraction of the aliphatic terpenic chlorides consists of linalyl chloride, since in the absence of geranyl chloride the alcohols obtained could only have been formed in the process of saponification of linalyl chloride with partial allylic rearrangement.

The cyclic terpenic chloride fraction (3rd fraction), after elimination of residues of geranyl chloride, gave a 90% yield of a terpenic chloride whose constants corresponded to those of α-terpinyl chloride [9, 10]. On saponification it gave crystalline α-terpineol with m.p. 34.5°. This result affords further confirmation of the formation of α-terpinyl chloride on telomerization of isoprene with its hydrochlorides [2].

The presence of the dihydrochloride of an aliphatic terpene (4th fraction) in the mixture – a dimer of the initial terpene hydrochlorides – is evidence that telomerization of isoprene with its hydrochlorides is accompanied by addition of the chlorides to the allylic double bonds of the chlorides themselves (10%). It follows that a large excess of the halogen derivative cannot be taken in order to obtain good yields of the primary products of addition of the allylic type to isoprene (geranyl and linalyl chlorides) for the purpose of increasing the velocity of the first stage of the telomerization reaction [1, 14]. If this is done, the velocity of formation of the dimers of the chlorides would also increase. The desired objective is achieved in satisfactory fashion by the previously proposed cleavage reaction [1, 2].

It is necessary to point out that only one of the chlorine atoms in the dichloride molecule undergoes saponification (Fig. 1).

Attempts to rectify the mixture of terpenic chlorides without preliminary elimination of geranyl chloride were unsuccessful, since partial decomposition occurred with evolution of hydrogen chloride. Most of the geranyl chloride broke down.*

Analysis of the resulting fractions showed, however, a fairly high content of easily saponifiable chlorine. This points to partial isomerization of geranyl chloride to linalyl chloride during slow distillation. On this basis, the method of preparation of pure linalyl chloride described below was developed.

A low boiling fraction containing a mixture of linalyl and lavandulyl chlorides was separated from the mixture of terpenic chlorides by rapid rectification, so that the residue in the still consisted of all of the remaining chlorides – geranyl chloride, terpinyl chloride and dichlorides. The residue was thereupon heated to 120-130° in a still with an efficient column and a solid condensation head, the fraction with b.p. 58-62° (4 mm) being slowly collected. Redistillation of the distillate gave three fractions. The first of these was enriched in terpenic hydrocarbons, the second (the main fraction) contained a low-boiling aliphatic terpenic chloride free of geranyl chloride and difficulty saponifiable lavandulyl chloride, as was established by the above-noted analysis for primary allylic chloride and easily saponifiable chloride.

Saponification of this terpenic chloride converted it into a mixture of terpenic alcohols – linalool and geraniol. Hence it follows that this chloride can only be linalyl chloride. The properties of the isolated terpenic chloride are set forth in the table (Compound I). They are similar to those of the low boiling, easily saponifiable portion of the fraction of aliphatic terpenic chlorides obtained after removal of geranyl chloride (Fig. 1) and identified as linalyl chloride.

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* In the course of 24-hours' rectification at a still temperature of 110-130°, the geranyl chloride content of the distillate fell from 55 to 8%.

The constants of the isolated linalyl chloride do not agree with the constants reported for this product by other authors [6, 7, 11].

A definite regularity in the physical properties of these substances can be discerned on comparing literature data for the lower isoprenoid, allylic halogenated derivatives and alcohols [15-17, 25] as well as for their homologs [18, 19]: 1) The tertiary alcohols and chlorides always possess lower refractions, densities and boiling points than the corresponding primary isomers; 2) chloro derivatives have slightly higher refractive indices than the corresponding hydroxy derivatives; the refractive index of a tertiary chloride is always lower than that of the corresponding primary alcohol. These regularities definitely do not apply, however, to the literature constants for geraniol, linalool, geranyl chloride and linalyl chloride in relation to linalyl chloride [7, 11, 20, 21]. This discrepancy, coupled with the fact that other authors did not make a careful check of the purity of the specimens of linalyl chloride that they isolated (especially with reference to the absence of geranyl chloride), justify the conclusion that all of the previously published data for the preparation of pure linalyl chloride are erroneous and that the authors of earlier investigations worked with mixtures of isomeric terpenic chlorides. By contrast, the sample of linalyl chloride prepared in the present work was free of isomeric terpenic chlorides, and its constants fit in satisfactorily with the regularities noted above. Its preparation by isomerization of geranyl chloride on slow distillation of the latter is readily accounted for by the shift in the equilibrium of the system geranyl chloride $\rightleftharpoons$ linalyl chloride due to removal of the lower-boiling linalyl chloride. A similar transformation of primary allylic chlorides into tertiary on slow distillation has already been reported by other investigators [18].

Attention must be directed to the behavior during saponification of the linalyl chloride isolated by the author. According to the literature [11, 21, 4] the saponification of linalyl and geranyl chlorides yields only linalool. In the present work, however, in which the conditions were somewhat different from those detailed in the literature, linalyl chloride yielded a mixture of geraniol and linalool (1 : 1).

Great interest is consequently attached to the further study of methods of preparation of the individual pure terpenic chlorides and their transformation into hydroxy derivatives. These investigations would impart precision to existing ideas about allylic rearrangements.

EXPERIMENTAL

1. Isolation of residual terpenic chlorides from the C_{10} telomer fraction. A study was made of the mixture of terpenic chlorides prepared by the previously described method [1, 2]. The yield of C_{10} fraction with b.p. 60-90° (2 mm) and $n^{20}D$ 1.474-1.481 was 45-50% (reckoned on the telomerization product); in different experiments its geranyl chloride content varied between 52 and 56% (as determined with hexamethylenetetramine in presence of KI [12]). The fraction under investigation contained 54.3% of geranyl chloride.

Into a 10-liter apparatus, fitted with a stirrer, were charged 1.85 kg of the fraction of terpenic chlorides, 0.85 kg hexamethylenetetramine and 10 kg dichloroethane (previously dried). After 50-hours' stirring at 20-23°, the compound of geranyl chloride with hexamethylenetetramine was extracted with water,* and the solution of the residual chlorides in dichloroethane was washed again with water, then with 10% NaCl solution and dried over K_2CO_3. The dichloroethane was distilled off, and the residue was distilled in vacuo to give 795 g of residual terpenic chlorides with a geranyl chloride content of 2.8%. The chlorides were subjected to fractional distillation (at 4 mm) in a 15-20-plate column packed with single-spiral glass helices (2.8 mm). The reflux number was maintained at 12-25 and the temperature in the still at 100-140°. The fractions were analyzed for refractive index, density, total chlorine (Pringsheim method), geranyl chloride (by reaction with hexamethylenetetramine in presence of KI [12]), saponifiable chloride (by boiling with alcoholic $Pb(NO_3)_2$ for 5 hours [1]), easily saponifiable chlorine (by saponification of a weighed sample of chloride in an emulsion with aqueous $NaHCO_3$ at 20° for 24 hours – for details see 2c below), and double bonds (Kaufmann method, reaction time 4 hours). Results of fractionation and analyses are plotted in Figure 1. For convenience the contents of chlorine and double bonds are expressed in milligram-equivalents per gram of substance.

2. Study of the kinetics of saponification of the fraction of lower-boiling aliphatic chlorides (2nd fraction). a) Saponification with lead carbonate in presence of an aqueous acetone solution of lead nitrate at 60°. Into a 100-ml flask, with a reflux condenser attached by a ground-glass fitting, were charged a weighed sample

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* Citral was obtained in 75% yield from the aqueous solution of the compound of geranyl chloride with hexamethylenetetramine under the previously described conditions [2].

of chloride (0.5 g), 5 ml 25% aqueous solution of lead nitrate, 5 ml 6% aqueous solution of $NaHCO_3$, and 25 ml acetone. The flask was heated on a water bath at the boil for a definite period; it was then cooled and addition was made of 10 ml 0.5 N nitric acid; after the precipitate had dissolved, 10 ml 10% NaCl solution was run in. The mixture was back-titrated with 0.5 N NaOH in presence of Bromphenol blue. A blank experiment without chloride was run in parallel. From the results of the two experiments the quantity of chloride entering into reaction was determined.

b) Saponification with sodium bicarbonate in aqueous acetone solution at 60°. A weighed quantity (0.5 g) of the substance, 10 ml 3% aqueous sodium bicarbonate solution and 15 ml acetone were put into a 100-ml flask. The mixture was boiled on a water bath for a determined time, cooled, and back-titrated with 0.5 N hydrochloric acid in presence of Bromphenol blue. The quantity of reacted chlorine was found in the same way as in the preceding experiment.

c) Saponification with aqueous solution of sodium bicarbonate in an emulsion at 20°. A 100-ml flask (ground-glass stopper) contained a weighed sample of chloride (0.5 g), 20 ml 1.5% aqueous $NaHCO_3$ solution and 0.1-0.2 g sodium salts of high-molecular alkylsulfuric acids (emulsifying agent). The flask was shaken on a machine for a determined time and the contents were back-titrated with 0.5 N HCl in presence of Bromphenol blue. The quantity of reacted chlorine was found as in the preceding experiments.

Results are presented in Figure 2.

3. Resolution of the low-molecular terpenic chlorides fraction (2nd fraction) by fractional saponification. 50 g $PbCO_3$, 50 ml 25% aqueous solution of $Pb(NO_3)_2$ and 200 ml acetone were placed in a round-bottomed flask fitted with mechanical stirrer, reflux condenser and dropping funnel. The mixture was heated to the boil, and a solution of 55.8 g chlorides (b.p. 61-64° (4 mm), d^{20}_4 0.910-0.913) in 50 ml acetone was added through the dropping funnel. After 40 minutes the boiling mixture was cooled, and 100 ml 10% NaCl solution and 1 ml pyridine were added. The acetone was distilled off on a water bath, and the product was distilled with steam, washed with water and dried over potassium carbonate to give 50.5 g saponification product containing 58% chlorides (formula $C_{10}H_{17}Cl$ on basis of the chlorine content) and 40% alcohols (Terent'ev determination).

To 46 g saponification product were added 41 g butyl borate and 0.5 g K_2CO_3. The butyl alcohol was distilled off and the residue was distilled in vacuo to give the difficultly saponifiable chloride (22 g) whose properties are set forth in the table (lavandulyl chloride). *

Saponification of the isolated chloride by boiling in aqueous acetone solution of lead nitrate in presence of lead carbonate (see above) for 60 hours gave a 67% yield of primary alcohol (found 97% $C_{10}H_{18}O$ by phthalation in pyridine after purification via the acid phthalic ester [23]).

B.p. 88° (10 mm), d^{20}_4 0.8740, $n^{20}D$ 1.4664, MR_D 48.92, bromine number 207.3. $C_{10}H_{18}OF_2$.
Calculated MR_D 48.87, bromine number 207.

Literature data for lavandulol [22]: b.p. 94-95° (13 mm), d^{17}_4 0.8785, $n^{17}D$ 1.4683.

After distillation of the lavandulyl chloride (b.p. 64.5° at 4 mm) and the excess of butyl borate (b.p. 88° at 4 mm), the residue of borates was decomposed by addition of aqueous $NaHCO_3$. After steam distillation, the alcohols were distilled in vacuo to give 13.6 g of a mixture of alcohols containing 41.8% of primary alcohols (as determined by phthalation in pyridine).

The mixture of alcohols was fractionated by reaction with phthalic anhydride in benzene [23]. The reaction was performed in presence of excess of pyridine at the boiling point of benzene in order to avoid dehydration of the tertiary alcohols by the resulting acid phthalic esters. The duration of the reaction was 6 hours.

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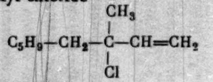
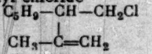
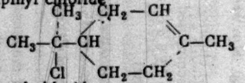
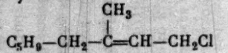
*Procedure b was employed for study of the kinetics of saponification of the individual chlorides (see 2b above). The velocity constants of saponification for the various reaction steps were found from the equation

$$k = \frac{2,3}{t_1 - t_2} \lg \frac{a_0 - a_1}{a_0 - a_2},$$

where a_0 is the amount of chlorine in the sample of chloride; a_1 is the quantity of chlorine entering into reaction in time t_1; a_2 is the quantity of chlorine reacting in time t_2. Results are presented in the table.

Physical and Chemical Properties of Individual Terpenic Chlorides of the C_{10} Fractions of the Telomer of Isoprene with its Hydrochlorides

Compound number	Name of formula	Boiling point (4 mm)	d_4^{20}	n_D^{20}	MR_D		% Cl		Bromine number (Kaufmann)		Saponifiable chlorine (% of total)		Velocity constant of the reaction K · 10^3 (sec^{-1})		Percent of terpene chlorides fraction
					found	calculated	found	calculated	found	calculated	in emulsion of aq. $NaHCO_3$ solu., 20° for 24 hr (easily saponif. cl)	in aq. alcoholic solu. of $Pb(NO_3)_2$ at 85°, 5 hr. (saponifiable cl)	of saponification with acetone solu. $NaHCO_3$ at 60°	with KI* (saturated solution in acetone) at 20°	
(I)	Linalyl chloride  $C_5H_9-CH_2-\overset{\overset{CH_3}{\mid}}{\underset{\underset{Cl}{\mid}}{C}}-CH=CH_2$	61°	0.9044	1.4654	52.77	52.31	19.82	20.53	186.5	185	100	100	> 200	Does not react	7—8
(II)	Lavandulyl chloride  $\underset{\underset{CH_3-C=CH_2}{\mid}}{C_5H_9-CH}-CH_2Cl$	64.5	0.9130	1.4683	52.61	52.31	20.50	20.53	181.7	185	3.3	83.5	1.855— 1.860	Does not react	9—10
(III)	Terpinyl chloride 	74.5	0.9730	1.4835	50.69	50.58	20.40	20.53	99.0	92.5	16.5	100	45—55	Does not react	18—20
(IV)	Geranyl chloride  $C_5H_9-CH_2-\overset{\overset{CH_3}{\mid}}{C}=CH-CH_2Cl$	75—80	—	—	—	52.31	—	20.53	—	185	100	100	> 200	38.4—40.0	52—56
(V)	Dihydrochloride of the aliphatic terpene $C_{10}H_{18}Cl_2$ |=	90—92	1.0245	1.4795	57.80	57.65	32.1	33.1	83.0	76.4	4.0	52.0	5.0 **	Does not react	9—10

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* Determined with hexamethylenetetramine [12].

** Calculated for saponifiable chlorine.

After boiling of the caustic alkaline extract for an hour and steam distillation, a primary alcohol (yield 98% $C_{10}H_{18}O$ by phthalation in pyridine) with the odor of geraniol was obtained.

B. p. 62-65° (1 mm), d^{20}_4 0.8834, $n^{20}D$ 1.4735; MR_D 49.02, bromine number 205.3. $C_{10}H_{18}OF_2$.
Calculated: MR_D 48.87, bromine number 207.

After purification via the calcium chloride compound [24], the isolated alcohol had the following constants:

B.p. 108-110° (10 mm), d^{20}_4 0.8802, $n^{20}D$ 1.4760. Literature data for geraniol [20]: b.p. 107° (8 mm), d^{20}_4 0.8830, $n^{20}D$ 1.4768.

The benzene solution of the alcohols not entering into reaction with phthalic anhydride was purified via the borate [13] and distilled in vacuo to give a tertiary alcohol (96% $C_{10}H_{18}O$ found by the Terent'ev method).

B.p. 78-80° (10 mm), d^{20}_4 0.8630, $n^{20}D$ 1.4614, MR_D 49.39, bromine number 200.3. $C_{10}H_{18}OF_2$. Calculated: MR_D 48.87, bromine number 207. Literature data for linalool [21]: b. p. 86-87° (14 mm), d^{20}_4 0.8622, $n^{20}D$ 1.4611.

4. Isolation of α-terpinyl chloride. 77.3 g of the fraction containing cyclic terpenic chlorides (III) was heated on a water bath with 7.7 g hexamethylenetetramine in solution in 120 ml methylene chloride for 6 hours in order to eliminate the residues of geranyl chloride (6%). The product was washed with water, the methylene chloride was distilled off, and the residue was distilled in vacuo to give α-terpinyl chloride (70 g) whose properties are set forth in the table (Compound III).

The latter was saponified for 10 hours in a boiling aqueous acetone solution of lead nitrate in presence of lead carbonate. The product was distilled with steam and purified via the boric ester (see above). In this way D,L-α-terpineol was obtained: m.p. 34°; no depression of melting point in admixture with an authentic preparation [20]. B.p. 94.5° (10 mm), d^{20}_4 0.9342, $n^{20}D$ 1.4815.

5. Preparation of pure linalyl chloride by isomerization of geranyl chloride. 660 g of terpene chlorides fraction containing 54.3% geranyl chloride was charged into the still of the column described above. With a still temperature of 100-110° and a reflux number of 7, 153.4 g of a mixture of low-boiling terpenic chlorides came over at 4 mm until the vapor temperature had risen to 68° and the $n^{20}D$ of the condensate had risen to 1.4705. The duration of the distillation was 6 hours.

Fractionation of the distillate by the method described above (see 3) gave lavandulyl chloride with the constants set forth in the table, geraniol and linalool.

The still temperature was subsequently raised to 120° and the reflux number was adjusted to give a fraction with b.p. 58-62° (4 mm), the $n^{20}D$ rising to 1.4760. Duration of distillation 30 hours at a reflux number of 20-25 and a still temperature of 120-130°.

The resulting fraction (182.4 g) was again fractionated in the same column. The following fractions were obtained from 146.3 g:

1st, terpenic hydrocarbons, 21.8 g. B.p. 44-54° (5 mm), d^{20}_4 0.816-0.831, $n^{20}D$ 1.473-1.481. Found %: Cl 0.21.

2nd, aliphatic terpenic chloride, 65 g. B.p. 58-62.3° (4 mm), d^{20}_4 0.890-0.901, $n^{20}D$ 1.466-1.467, bromine number 192.

Found %: Cl 18.6. $C_{10}H_{17}Cl$. Calculated %: Cl 20.53.

3rd, terpinyl chloride, 32 g with a 19% content of geranyl chloride. B.p. 69-76° (4 mm), d^{20}_4 0.947-0.954, $n^{20}D$ 1.478-1.481, bromine number 118. Residue, 20 g.

Redistillation of the 2nd fraction yielded linalyl chloride (38 g) with the properties set forth in the table. Saponification of 30 g of the chloride for 30 minutes under the conditions described above (see 3) gave 22 g of a mixture of alcohols containing 45% primary alcohols. Geraniol and linalool were isolated by resolution with the help of phthalic anhydride.

Geraniol: b.p. 94-96° (5 mm), d^{20}_4 0.8800, $n^{20}D$ 1.4762, bromine number 206.3.
Linalool: b.p. 65-67° (5 mm), d^{20}_4 0.8611, $n^{20}D$ 1.4620, bromine number 205.2.

SUMMARY

1. The composition of the fraction of terpenic chlorides (C_{10}) from the product of telomerization of isoprene with its hydrochlorides in presence of anhydrous stannic chloride was studied.

2. A study of the kinetics of interaction of the mixture of chlorides with various reactants led to a scheme for separation of the C_{10} fraction into individual isomers and their derivatives. Analytical techniques for determination of the purity of the individual isomeric chlorides were also worked out.

3. Apart from geranyl chloride (52-56%) and α-terpinyl chloride (18-20%) which were previously found, the C_{10} fraction contains linalyl chloride (7-8%), lavandulyl chloride (9-10%) and the dimer of the original isoprene hydrochlorides (9-10%).

4. Telomerization of isoprene with its hydrochlorides is accompanied by 1,2-, 1,4- and 3,4-addition (the latter not in accordance with the Markovnikov rule) of the chlorides to isoprene. At the same time we find cyclization and allylic dimerization of the chlorides.

5. In the telomerization of isoprene with halogenated derivatives, allylic products of addition can only be obtained in satisfactory yield with the help of the previously proposed cleavage reaction.

6. Pure lavandulyl chloride and α-terpinyl chloride were isolated from the C_{10} fraction.

7. Slow distillation at 120-130° of the geranyl chloride of the C_{10} fraction causes partial isomerization to linalyl chloride and partial dehydrochlorination with formation of terpenes.

8. A method of preparation of pure linalyl chloride from the C_{10} fraction was developed. It involved isomerization of the geranyl chloride present.

9. The constants of the prepared linalyl chloride are presented, and all of the previously published methods for its preparation and the constants previously reported are critically discussed.

10. Saponification of linalyl chloride under the conditions of investigation gave a 1 : 1 mixture of geraniol and linalool.

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THE CONDENSATION OF 1-HEPTYNE WITH CHLORAL

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It has long been known that chloral in presence of various condensing agents is capable of entering into reaction with aromatic compounds, with formation (depending on the conditions) of aryltrichloromethylcarbinols $ArCh(OH)CCl_3$ (I) or diaryltrichloroethanes $ArCH(CCl_3)Ar$ (II) [1].

Colonge recently showed [2] that chloral can similarly be condensed with olefinic hydrocarbons of the the aliphatic and alicyclic series with formation of condensation products of type (I).

We were investigated in extending this reaction to acetylenic hydrocarbons with a terminal triple bond, since the products of such a condensation – trichloromethylalkynylcarbinols – may find applications in organic synthesis. With this objective we condensed chloral with 1-heptyne which is obtainable with relative facility from enanthaldehyde [3]. In presence of basic condensing agents (sodium carbonate and sodium hydroxide), likewise sulfuric acid, no condensation occurred, the acetylenic hydrocarbon being recovered unchanged from the reaction mixture. In presence of $AlCl_3$, however, we observed the formation of a product whose analysis corresponded to 1,1,1-trichloro-3-nonyn-2-ol., $CH_3(CH_2)_4C \equiv CCH(OH)CCl_3$.

The reaction product also contained a crystalline substance, apparently 1,1,1,4-tetrachloro-3-nonen-2-ol, and a minute quantity of a substance not containing a labile hydrogen and corresponding (judging by the chlorine content and the molecular weight) to 1,1-dichloro-2-(heptyn-1'-yl)-ethylene oxide. The latter oxide could be formed by cleavage of HCl from the normal product of condensation. The possibility of such transformations of trichlorocarbinols was noted by Iu. S. Zalkind in the case of chloral-acetone [4].

Trichloromethylcarbinol was also formed on condensation of chloral with 1-heptyne in presence of BF_3. 1,1,1,2-Tetrachloro-3-nonen-2-ol was then not detected among the reaction products.

Our condensation product whose analysis corresponded to 1,1,1-trichloro-3-nonyn-2-ol was subjected to hydrolysis both in an acid and an alkaline medium. It is known that hydrolysis of such trichloromethylcarbinols is accompanied by secondary reactions. The corresponding α-hydroxy acid is formed in the main reaction (hydrolysis of the trichloromethyl group) [5], but this is accompanied by cleavage to chloroform and aldehyde [6-8] and breakdown to the original components [8].

Colonge [8] points out that the products of condensation of chloral with olefinic hydrocarbons are less susceptible to cleavage into chloroform and aldehyde than the corresponding saturated trichloromethylcarbinols. According to his findings olefinic trichloromethylcarbinols with a long carbon chain, for example 1,1,1,-trichloro-3-nonen-2-ol, do not form aldehydes at all under such conditions. At the same time, similar trichloromethylcarbinols with fewer substituents in the chain are extremely susceptible to breakdown into the original components.

We treated our product of condensation of chloral with 1-heptyne with solutions of the following reagents: K_2CO_3, Na_2CO_3, $Ba(OH)_2$, NaOH (aqueous and alcoholic), and concentrated H_2SO_4. In no case did we observe the formation of the corresponding α-hydroxyacid or of an aldehyde of the acetylenic series (breakdown with separation of chloroform). No hydrolysis takes place when using K_2CO_3, Na_2CO_3 or $Ba(OH)_2$, and the original trichlorocarbinol is recovered. Concentrated H_2SO_4 causes severe resinification. With aqueous or alcoholic NaOH we obtained methyl amyl ketone and a mixture of acidic substances. Formation of the ketone indicates breakdown of the product of condensation into the original components and hydration of the acetylenic hydrocarbon. No pure substances could be separated from the mixture of acids by fractionation in vacuo. The analytical data (content of chlorine and hydroxyl groups and bromine and acid numbers) indicate that the acidic fraction is probably a mixture of an unsaturated acid and a chloroacid which is not amenable to fractionation. It was therefore not further investigated.

EXPERIMENTAL

Condensation of 1-heptyne with chloral. To a mixture of 22 g heptyne,* 60 ml dichloroethane and 30 g chloral free of chloral hydrate (determined aquametrically [10])was added 4 g $AlCl_3$ at room temperature in the course of 1 hour. The reaction mixture was thereupon stirred for another hour and poured into cold water. The separated products were extracted with ether. After thorough washing with 10% NaOH solution followed by water, drying with Na_2SO_4 and removal of the solvent, the residue was distilled in vacuo. Two fractions were collected as the result of three distillations: 1st, b. p. 106-110° (4 mm), 15.7 g (41.2% calculated on original 100% 1-heptyne); 2nd, b. p. 115-125° (4 mm), 5.8 g (partially crystallizing on standing).

The 1st fraction had the following constants:

B. p. 106-110° (4 mm), $n^{20}D$ 1.5040, d^{20}_4 1.2294, MR_D 58.64; calc. 57.88.

Found %: C 44.23; H 5.63; Cl** 43.60; OH*** 6.55. $C_9H_{12}(OH)Cl_3$. Calculated %: C 44.35; H 5.35; Cl 43.73; OH 6.9.

The 2nd fraction was spread on a porous plate and gave 3.2 g (7.6%) colorless crystals with m. p. 61°. This product did not darken on prolonged storage; readily soluble in alcohol, acetone, benzene, chloroform, ligroine and cyclohexane; insoluble in water even on boiling.

Found %: C 38.91, 38.91; H 5.07, 4.84; Cl 49.88; OH 5.96. M 267 (cryoscopically). $C_9H_{13}(OH)Cl_4$. Calculated %: C 38.57; H 5.00; Cl 50.70; OH 6.07. M 280.

A liquid substance was also isolated, in separate experiments, from the lower-boiling fractions:

B. p. 114° (10 mm), $n^{20}D$ 1.500, d^{20}_4 1.2159, MR_D 50.07; calc. 50.92.

Found %: Cl 33.8. M 213. $C_9H_{12}OCl_2$. Calculated %: Cl 34.29. M 207.

A Tserevitinov determination in this case revealed complete absence of mobile hydrogen (determined, 0.77% OH groups).

Condensation of 1-heptyne with chloral in presence of BF_3. BF_3**** was passed into a mixture of 45 g heptyne and 60 g chloral in 60 g dichloroethane for 15 minutes with good stirring. The temperature in the reaction mixture was maintained at 20-25°; the weight increase was 10 g. The reaction mass was stirred for another 1 hour and then poured into water. The separated product was extracted with ether; the ethereal solution was washed twice with 10% NaOH solution, then with saturated NaCl solution and dried with Na_2SO_4. The solvent was removed, and the residue distilled in vacuo. After two distillations, there was obtained 41 g (50%) of product.

B. p. 107-109° (3 mm), $n^{20}D$ 1.4930, d^{20}_4 1.2298, MR_D 57.42; calc. 57.88.

Found %: C 44.02, 44.00; H 5.62, 5.76; Cl 43.0; OH 6.5. $C_9H_{12}Cl$ (OH). Calculated %: C 44.35; H 5.35; Cl 43.73; OH 6.9.

Action of aqueous NaOH solution on 1,1,1-trichloro-3-nonyn-2-ol. 35 g trichlorocarbinol was boiled for 1 hour with 250 ml 10% aqueous sodium hydroxide solution. The alkaline solution was extracted 3 times with ether. The extract was worked up in the usual manner, the solvent was removed, and two distillations gave 3.0 g (15.6%) of methyl amyl ketone.

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* Heptyne prepared from enanthaldehyde [3] had b. p. 100-120°, $n^{20}D$ 1.4170, d^{20}_4 0.7554. It contained 68% of 1-heptyne (determined through the Ag derivative) [9].

** Chlorine was determined with a skeletal nickel catalyst [11].

*** Determined by Tserevitinov method.

**** Prepared by heating of a mixture of KBF_4, B_2O_3 and H_2SO_4 [12].

B. p. 150-153°, $n^{20}D$ 1.4080, d^{20}_4 0.8147, MR_D 34.42; calc. 34.53.

Ketone content * 93.8%. Semicarbazone, m. p. 120-121°. A mixture with the semicarbazone of authentic methyl amyl ketone did not show a depression of m. p.

Found %: N 24.48, 24.44. $C_8H_{17}ON_3$. Calculated %: N 24.56.

Acidification of the alkaline solution gave 7 g of a mixture of acidic substances from which the following fraction was isolated in vacuo:

B. p. 137-140° (4 mm), $n^{20}D$ 1.5225, d^{20}_4 1.089. Acid number 303.5; bromine number 89.9. Found %: Cl 13.25.

SUMMARY

1. It was shown that chloral condenses with 1-heptyne in presence of $AlCl_3$ or BF_3 to form the corresponding trichloromethylcarbinol. In presence of $AlCl_3$ additional products are 1,1,1,4-tetrachloro-3-nonen-2-ol and a compound not containing a mobile hydrogen atom – apparently 1,1-dichloro-2-(heptyn-1'-yl)-ethylene oxide.

2. Alkaline hydrolysis of the product of condensation of 1-heptyne with chloral gave methyl amyl ketone in addition to a fraction apparently consisting of a mixture of an unsaturated acid and chloroacid which could not be separated into its constituents and was not further examined.

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REDUCTION OF DERIVATIVES OF HARMINE WITH SODIUM BOROHYDRIDE TO DERIVATIVES OF Py-TETRAHYDROHARMINE

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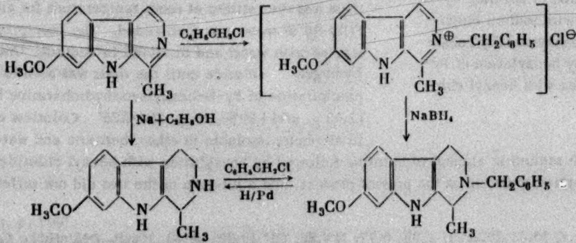
The problem of converting the pyridine ring of harmine into the 1,2,5,6-tetrahydropyridine ring arose in the course of work on the synthesis of analogs of reserpine on the basis of harmine. The reduction of harmine to Py-tetrahydroharmine by sodium in alcohol has been described in the literature [1]. This method is inconvenient because it requires a very large excess of sodium (12 times the weight of the harmine). Moreover, the method was found to be inapplicable to Py-quaternary derivatives of harmine [2]. Experiments on the reduction of the latter with zinc dust in dilute acetic acid, likewise catalytically with platinum in anhydrous alcohol and in glacial acetic acid at 80°, were unsuccessful [2].

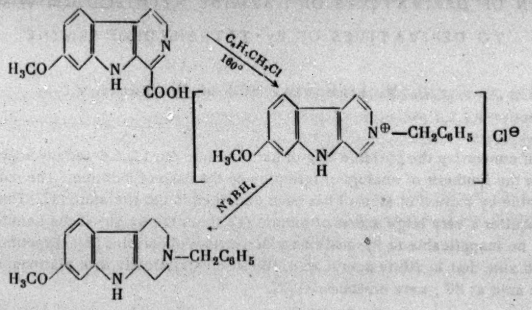
Various methods of conversion of harmine derivatives into derivatives of Py-tetrahydroharmine were studied, and we established that the best reducing agent in this case is sodium borohydride. It was shown that only quaternary salts of harmine undergo reduction. Harmine itself and its nonquaternary derivatives do not react with sodium borohydride. Consequently, when it is necessary to prepare derivatives of Py-tetrahydroharmine which are not substituted at the Py-nitrogen, harmine Py-N-benzyl chloride is reduced, and later the benzyl group is removed by hydrogenation of the Py-N-benzyltetrahydroharmine over palladium catalyst. Harmine Py-N-benzyl chloride is obtained in 95% yield by heating equimolar quantities of harmine and benzyl chloride in benzyl alcohol at 120° for 12 hours. Reduction of harmine Py-N-benzyl chloride is effected in methyl alcohol with sodium borohydride, which is added portionwise at room temperature. The reaction duration is 3 hours. Yield of Py-N-benzyltetrahydroharmine hydrochloride is 90%.

Py-N-Benzyltetrahydroharmine was also synthesized from harmine by another route. Harmine was reduced with sodium in alcohol by Fischer's method [1] to form Py-tetrahydroharmine. The latter was subjected to benzylation with benzyl chloride in presence of potassium carbonate at 110-120°. The resulting Py-N-benzyltetrahydroharmine (yield 78%) was identical with the product of reduction of harmine Py-N-benzyl chloride with sodium borohydride. The two compounds had the same constants and solubilities, did not show a depression of melting point in a mixed test, and exhibited identical analyses and ultraviolet spectra (see diagram).

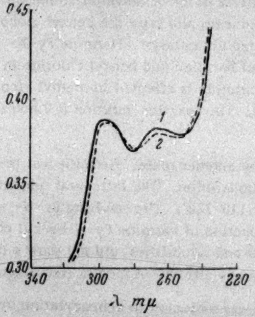
Py-N-Benzyltetrahydroharmine, obtained by borohydride reduction, was subjected to debenzylation by hydrogenation over palladium catalyst. The resulting Py-tetrahydroharmine (yield 96.4%) was found to be identical with the product of reduction of harmine with sodium in alcohol.



Similar results were obtained in work with derivatives of norharmine. In this case the starting substance was norharmine-3-carboxylic acid, which was synthesized by the method of Perkin and Robinson [3]. Norharmine-3-carboxylic acid remains unchanged when heated with benzyl chloride in benzyl alcohol to 120°. Further rise of temperature leads to commencement of decarboxylation and simultaneous formation of the Py-quaternary salt. A mixture of the original norharmine-3-carboxylic acid and norharmine Py-N-benzyl chloride is formed in the 120-160° temperature range. At 160° the main product of the reaction (yield 53%) is norharmine Py-N-benzyl chloride. The latter is reduced by sodium borohydride in methyl alcohol at room temperature with formation of Py-N-benzyltetrahydronorharmine in 95% yield.



EXPERIMENTAL



Ultraviolet absorption spectra.
1) Py-N-benzyltetrahydroharmine obtained by reduction of harmine Py-N-benzyl chloride with sodium borohydride; 2) Py-N-benzyltetrahydroharmine obtained by benzylation of Py-tetrahydroharmine with benzyl chloride.

Harmine Py-N-benzyl chloride. 2.1 g harmine and 1.3 g benzyl chloride were heated at 120° for 12 hours in 80 ml benzyl alcohol. During the reaction the whole of the harmine went into solution. Removal in vacuo of the benzyl alcohol left a thick mass which crystallized on trituration in presence of ether. Recrystallization from isopropanol gave 3.16 g (95%) harmine Py-N-benzyl chloride. Colorless crystals, m. p. 237-238°. Readily soluble in chloroform, methanol and hot isopropanol; insoluble in ether, water, ethyl acetate and benzene; poorly soluble in acetone and dioxane.

Found %: N 7.95, 8.51; Cl' 10.40, 10.14. $C_{20}H_{19}ON_2Cl$. Calculated %: N 8.27; Cl' 10.48.

Py-N-Benzyltetrahydroharmine hydrochloride. a) Reduction of harmine Py-N-benzyl chloride with $NaBH_4$. In the course of 30 minutes 1.5 g sodium borohydride was added portionwise to a solution of 1.2 g harmine Py-N-benzyl chloride in 50 ml methanol. Foaming and heating occurred during the reaction. The reaction mass was then stirred at room temperature for another 2.5 hours. Fifty ml of water was then added. The precipitate was filtered, washed with water and dissolved in acetone. Addition of alcoholic hydrogen chloride until the mass was acid to congo resulted in precipitation of Py-N-benzyltetrahydroharmine hydrochloride (1.09 g, yield 90%), m. p. 224-225° Colorless crystals, soluble in alcohols, insoluble in ether, benzene and water. The product of reduction with sodium in alcohol of harmine followed by benzylation with benzyl chloride had the same ultraviolet absorption spectrum as the present product, and a mixture of the two did not suffer a depression of melting point.

Found %: C 70.21, 70.20; H 6.86, 6.77; N 7.88; Cl' 10.39, 10.43. $C_{20}H_{22}ON_2 \cdot HCl$. Calculated %: C 70.07; H 6.72; N 8.17; Cl' 10.36.

b) Benzylation of Py-tetrahydroharmine. 2.12 g Py-tetrahydroharmine, prepared by reduction of harmine with sodium in alcohol, 1.3 g benzyl chloride and 2 g calcined potassium carbonate were heated in 30 ml toluene for 4 hours at 110-120°. The mass was then treated with 20 ml of water. The toluene was separated and the aqueous layer was extracted with chloroform. The chloroform-toluene solution was evaporated. The residue was recrystallized from a little methanol. Yield of Py-N-benzyltetrahydroharmine hydrochloride 1.9 g (78%); m. p. 224-225°.

Found %: C 69.72; H 6.43; N 8.28. $C_{20}H_{22}ON_2 \cdot HCl$. Calculated %: C 70.07; H 6.72; N 8.17.

Py-Tetrahydroharmine. 0.5 g Py-N-benzyltetrahydroharmine hydrochloride was reduced in 30 ml ethyl alcohol at 18-20° and a pressure of 20-30 cm water column with a palladium catalyst prepared from 0.5 g palladium chloride. Absorption of hydrogen was completed in the course of 3 hours. The catalyst was filtered off and the alcoholic solution was evaporated in vacuo. The residue was treated with 5 ml 20% sodium hydroxide solution, filtered and washed with water. Yield of Py-tetrahydroharmine 0.3 g (96.4%), m. p. 199°.* A mixture with Py-tetrahydroharmine obtained by reduction of harmine with sodium in alcohol did not undergo a depression of melting point.

Norharmine-Py-benzyl chloride. 2.52 g norharmine-3-carboxylic acid and 1.3 g benzyl chloride were heated in 100 ml benzyl alcohol for 5 hours at 160°. The acid gradually went into solution. At the same time carbon dioxide was evolved and the reaction mass darkened. The brownish, fluorescent solution was treated with 4 times the quantity of ether. A precipitate came down and was reprecipitated from methanol solution with acetone. It had m. p. 225-226°. Yield 2.5 g (53%) of colorless crystals of norharmine Py-benzyl chloride. Soluble in alcohols, poorly soluble in chloroform and acetone, insoluble in water, ether and benzene.

Found %: C 66.93, 66.81; H 5.28, 5.57; N 8.32; Cl' 10.97, 10.66. $C_{19}H_{17}ON_2Cl$. Calculated %: C 67.18; H 5.24; N 8.63; Cl' 10.94.

Py-N-Benzyltetrahydronorharmine. 0.7 g norharmine Py-benzyl chloride was reduced with 0.93 g sodium borohydride in similar fashion to the above-described reduction of harmine Py-N-benzyl chloride. The reaction was carried out in methanol. Py-N-Benzyltetrahydronorharmine came down on dilution of the methanol solution with twice the volume of water. Yield 0.6 g (95%). Colorless crystals, m. p. 170-170.5° (from methanol). Readily soluble in acetone and chloroform, less soluble in alcohols, benzene and toluene, insoluble in ether and water.

Found %: C 78.20, 78.07; H 6.75, 6.79; N 9.35, 9.43. $C_{19}H_{20}ON_2$. Calculated %: C 78.08; H 6.85; N 9.59.

SUMMARY

A method was developed for reduction of harmine derivatives to Py-tetrahydroharmine derivatives with sodium borohydride; yield 90-95%.

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*Literature [1]: m. p. 199°.

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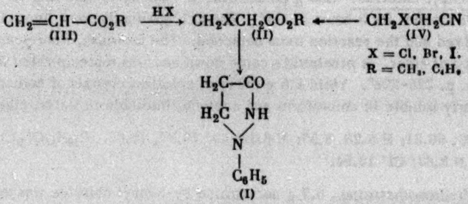
SYNTHESIS OF 1-PHENYL-3-PYRAZOLIDONE (PHENIDONE) FROM ESTERS OF β-CHLOROPROPIONIC ACID

V. N. Mikhailova and V. V. Pigulevskii

Esters of β-halopropionic acids (II) can serve as starting materials for the synthesis of 1-phenyl-3-pyrazolidone (I). These esters can be prepared from the corresponding esters of acrylic acid (III) by treatment with hydrogen halides, as well as from the nitriles of these acids [1].

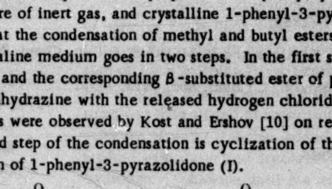


In the present investigation we synthesized 1-phenyl-3-pyrazolidone from esters of β-chloropropionic acid, and we carried out experiments on the synthesis of nitriles of β-bromo- and β-iodopropionic acids.

1-Phenyl-3-pyrazolidone is now extensively used in cinematography as a substitute for metol [2-5].

Phenidone was first synthesized from phenylhydrazine and a β-halopropionic acid or its esters [7]. The structure of 1-phenyl-5-pyrazolidone was erroneously assigned to the prepared substance (m. p. 121°), which according to the literature melts at 78° [7]. The structure of 1-phenyl-3-pyrazolidone was demonstrated by synthesis from the ethyl ester of β-iodopropionic acid and aniline [8].

On checking Beringer's method [6] we found that condensation in a strongly alkaline medium is accompanied by considerable resinification, and the yield of 1-phenyl-3-pyrazolidone is extremely low. Its isolation from the oily reaction product is also very difficult. It was earlier shown [9] that resinification is not observed when equimolar quantities of methyl β-chloropropionate and phenylhydrazine are condensed in weakly alkaline medium in an atmosphere of inert gas, and crystalline 1-phenyl-3-pyrazolidone is formed in satisfactory yield. We established that the condensation of methyl and butyl esters of β-chloropropionic acid with phenylhydrazine in a weakly alkaline medium goes in two steps. In the first step, which has the higher velocity, hydrogen halide is released and the corresponding β-substituted ester of propionic acid (V) is formed. In addition, interaction of phenylhydrazine with the released hydrogen chloride gives phenylhydrazine hydrochloride. Similar transformations were observed by Kost and Ershov [10] on reaction of β-chloropropionitrile with phenylhydrazine. The second step of the condensation is cyclization of the ester of β(α-phenylhydrazino)-propionic acid (V) with formation of 1-phenyl-3-pyrazolidone (I).



The duration of the condensation reaction depends on the original ester of β-chloropropionic acid and on the conditions of condensation.

The synthesis of 1-phenyl-3-pyrazolidone from the methyl ester of β-chloropropionic acid goes more quickly than from the butyl ester, and the yield in the former case is larger (see Table). This probably due to the methoxy group splitting off with greater facility than the butoxy group during cyclization.

Conditions of Preparation of 1-Phenyl-3-pyrazolidone

Expt. No.	Esters of β-chloropropionic acid and their quantity	Phenylhydrazine (in g)	Total duration of reaction (hours)	Yield of 1-phenyl-3-pyrazolidone (%)
1•	Methyl, 5 g	4.3	20	45
2•	" " "	4.3	25	43.8
3•	" " "	4.3	30	46.5
4••	" 5.8 g	4.3	25	48
5•	Butyl 9.1 g	5.4	25	17.8
6•	" 9.1 g	5.4	30	17.8
7••	" 9.1 g	5.4	30	19.3
8••	" 9.1 g	5.4	50	19.3

• Experiments in a stream of nitrogen.

•• Experiments in an atmosphere of carbon dioxide.

The phenylhydrazine salt contaminates the main product of the reaction and is a hindrance to separation of the latter from the mixture. It was therefore necessary to remove the salt and to continue the reaction in an atmosphere of nitrogen or carbon dioxide.

With sulfuric acid or calcium hypochlorite, phenidone gives a very transitory pink coloration whose intensity depends on the concentration of 1-phenyl-3-pyrazolidone. These color reactions can evidently be used to check the course of the condensation.

Formation of an unstable colored substance on oxidation of 1-phenyl-3-pyrazolidone by certain oxidants is probably associated with formation of colored intermediate products, since the end product of oxidation of 1-phenyl-3-pyrazolidone is the colorless 1-phenyl-3-pyrazolone [7].

EXPERIMENTAL

1. Synthesis of methyl and butyl esters of β-chloropropionic acid. These were prepared from the corresponding acrylates and dry hydrogen chloride by the method that we previously developed [1, 11].

2. Synthesis of 1-phenyl-3-pyrazolidone (see Table.) a) From methyl β-chloropropionate and phenylhydrazine. Condensation of the methyl ester (b. p. 155-157°) with phenylhydrazine was performed on a boiling water bath in closed containers in a nitrogen atmosphere or in flasks with reflux condensers in a stream of carbon dioxide. Heating of the ester with phenylhydrazine for 10-15 minutes was followed by deposition of colorless scales (2.2 g) of phenylhydrazine hydrochloride with m. p. 240° (decomp.) [12]. The latter were filtered off after 2-2.5 hours.

Further heating of the filtrate with the wash liquor in an inert gas atmosphere led to formation of 1-phenyl-3-pyrazolidone in the form of colorless crystals which were identified by the calcium hypochlorite test (pink color). The reaction ended after 18-20 hours. After cooling, the colorless crystals were filtered off, washed with alcohol and ether, and dried in a vacuum-desiccator in the absence of daylight. The average yield of 1-phenyl-3-pyrazolidone with m. p. 120-121° was 45%.calculated on the reacted phenylhydrazine. Further heating of the mother liquor in an inert gas stream did not increase the yield of the product.

Similar results were obtained when the condensation was effected in round-bottomed flasks with stirrers and a reflux condenser in a stream of carbon dioxide. The yield of 1-phenyl-3-pyrazolidone was 48%.

b) From butyl β-chloropropionate. The above procedure was employed in this condensation.

Found %: C 66.79; H 6.38; N 17.40. M 159. $C_9H_{10}ON_2$. Calculated %: C 66.66; H 6.17; N 17.28. M 162.

1-Phenyl-3-pyrazolidone hydrochloride was prepared in quantitative yield by passage of dry hydrogen chloride through a solution of 1-phenyl-3-pyrazolidone in anhydrous alcohol. Colorless, lustrous crystals with m. p. 162-163°. The literature [7] reports m. p. 163°.

Found %: N 14.00; Cl 17.60. $C_9H_{10}ON_2HCl$. Calculated %: N 14.10; Cl 17.88.

2. Synthesis of nitriles of β-halopropionic acids. a) β-Bromopropionitrile was prepared by the same procedure as for β-chloropropionitrile [1]. A Tishchenko bottle containing a solution of phenol in carbon tetrachloride was inserted between the hydrogen bromide generator and the reaction vessel in order to remove bromine from the hydrogen bromide. Drying of the hydrogen bromide was effected by passage through a U-tube filled with phosphorus pentoxide. The purified and dried hydrogen bromide was cooled (0°) before introduction into the reaction vessel via a glass tube extending to the surface of the acrylonitrile. This arrangement was necessary to preclude choking of the glass tube with white crystals of $CH_2BrCH_2CN \cdot HBr$ [13]. After saturation with the equimolar quantity of hydrogen bromide (determined by the increase in weight), the yellow reaction mixture was left overnight at room temperature, and then washed with sodium sulfite and water, dried over anhydrous sodium sulfate, and twice fractionated in vacuo. Average yield 70-75%. β-Bromopropionitrile is a colorless, mobile, oily liquid with a fairly persistent and strong odor that does not irritate the mucous membranes; readily soluble in ether and acetone. It turns yellow on standing in the light, but in the dark it remains colorless for a long period.

B. p. 81-83° (15 mm), $n^{20}D$ 1.4750, d^{20}_4 1.6158, MR_D 23.33; calc. 23.52. Literature data [14]: b.p. 92° (25 mm), d^{20}_4 1.6152, $n^{20}D$ 1.1470.

Found %: Br 59.51; N 10.44. C_3H_4NBr. Calculated %: Br 59.70; N 10.70.

b) β-Iodopropionitrile was prepared in similar fashion to the preceding nitrile. Purified and dried hydrogen iodide was passed (cooling to 0°) into acrylonitrile until saturation occurred (1 : 1), and the reaction liquid then stood at room temperature in the dark for 15-20 hours. Reaction products were isolated in the same way as in the preceding experiment. Average yield of β-iodopropionitrile 35-40%. A fairly mobile, colorless, oily liquid with a persistent odor; readily soluble in acetone and ether.

B. p. 105-106° (9 mm), $n^{20}D$ 1.550, d^{20}_4 2.0377, MR_D 28.80; calc. 28.52. Literature data [15]: b. p. 101° (25 mm).

Found %: I 69.95; N 7.73. C_3H_4NI. Calculated %: I 70.16; N 7.61.

SUMMARY

1. 1-Phenyl-3-pyrazolidone was synthesized from methyl or butyl β-chloropropionate and phenylhydrazine in a weakly alkaline medium.

2. The nitriles of β-iodo- and β-bromopropionic acids, prepared from acrylonitrile and the corresponding hydrogen halide, were characterized.

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**In Russian.

THE SYNTHESIS OF 4-AMINOPIPERIDINE

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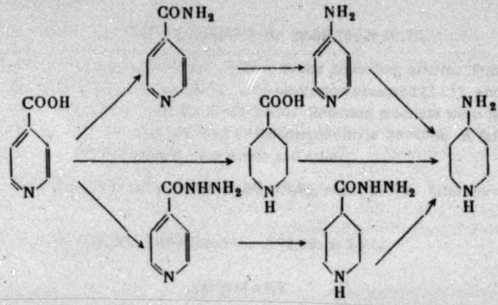
4-Aminopiperidine is an intermediate for the synthesis of biologically active substances. Prelog, Cerkovnikov and their co-workers [1] have shown that some N-substituted 4-aminopiperidines possess a spasmolytic action. At the same time the literature does not contain a convenient method of preparation of 4-aminopiperidine. This compound is synthesized either by reduction of 4-aminopyridine with sodium in alcohol [2] (yield not higher than 50%, i.e., 30% reckoned on the isonicotinic acid) or from acyclic compounds by multistep methods via tetrahydropyran derivatives (extremely low over-all yield) [1].

In the present paper we describe a convenient preparative method for obtaining 4-aminopiperidine dihydrochloride from isonicotinic acid in two steps with an over-all yield of 66%. Several routes to 4-aminopiperidine from isonicotinic acid were examined in the course of this work (in recent years isonicotinic acid has become a commercial product [3]).



The reactions of Hofmann, Curtius and Schmidt were used for conversion of the carboxyl to the amino group.

In the first variant, isonicotinic acid was converted by the published method [4] via the ester to the amide, and the latter by the Hofmann reaction to 4-aminopyridine. We know from the literature that attempts to catalytically reduce 4-aminopyridine to 4-aminopiperidine have been unsuccessful [2, 5]. Our experiments on hydrogenation of 4-aminopyridine in alcohol under pressure in presence of a platinum catalyst showed that hydrogen is not taken up to 1 to 60 atm. Hydrogenation proceeds only under a pressure of 80 atm, and a mixture of products was formed from which 4-aminopiperidine was isolated in 16.5% (reckoned on the 4-aminopyridine) or in 6% yield (reckoned on the isonicotinic acid). The possibility in principle of catalytic reduction of 4-aminopyridine to 4-aminopiperidine was thereby demonstrated.

In the second variant, isonicotinic acid was converted into the hydrazide via the ester by the published method [6]. The hydrazide was reduced in presence of platinum catalyst to the hydrazide of isonipecotic acid which had previously been obtained by a less convenient route – from the ethyl ester of isonipecotic acid and hydrazine hydrate. The hydrazide of isonipecotic acid was subjected to the Curtius reaction for conversion into 4-aminopiperidine. In the course of this reaction the formation of the azide was accompanied by nitrosation at the nitrogen of the piperidine ring. The resulting N-nitroso derivative of isonipecotic acid hydrazide is highly soluble in water and insoluble in organic solvents. Without being isolated, it was therefore converted into the urethane and then, by boiling with concentrated hydrochloric acid, into 4-aminopiperidine dihydrochloride. The yield of the latter was 20.6%, calculated on the isonicotinic acid.

It was found most convenient to prepare 4-aminopiperidine by reduction of isonicotinic acid to isonipecotic acid followed by replacement of the carboxyl group by amino in the Schmidt reaction. Catalytic hydrogenation of isonicotinic acid in dilute hydrochloric acid goes smoothly with quantitative yield and is more convenient than the literature method [7] of hydrogenation in a medium of glacial acetic acid followed by isolation of the isonipecotic acid in the form of the hydrochloride. The Schmidt reaction can be performed both with hydrazoic acid and with sodium azide in presence of sulfuric acid. The second method is more convenient on the preparative scale and does not involve prior isolation of poisonous hydrazoic acid. The yield of 4-aminopiperidine is 62% by the hydrazoic acid method and 66% by the sodium azide method.

The following N-formyl derivatives were also synthesized in the course of the work: 1-formylisonipecotic acid and 1-formyl-4-formylaminopiperidine.

EXPERIMENTAL

Preparation of 4-Aminopiperidine

A. From 4-aminopyridine. 3.45 g 4-aminopyridine in 120 ml anhydrous alcohol was treated with 9 ml alcoholic solution of hydrogen chloride. The resulting solution was placed in a glass container in a rotating autoclave and subjected to hydrogenation at 20° and a pressure of 80 atm. in presence of 0.2 g platinum catalyst prepared by Adams' method. After the calculated quantity of hydrogen had been absorbed, the reaction mass was treated with 20 ml water to dissolve the precipitated organic salts. The platinum was filtered off, and the filtrate was evaporated in vacuo to give 4.6 g of a mixture of hydrochlorides. Trituration of the latter in presence of 30 ml anhydrous alcohol led to separation of 0.6 g (16.5%) of 4-aminopiperidine dihydrochloride. Colorless crystals with m. p. 331-333°.*

Picrate. Light-yellow crystals. Insoluble in water and common organic solvents; soluble in hot alcohol; m. p. 245° (decomp.).

Found %: 36.88, 36.94; H 3.44, 3.54; N 19.69, 20.24. $C_5H_{12}N_2 \cdot 2C_6H_3O_7N_3$. Calculated %: C 36.56; H 3.23; N 20.07.

B. Via isonipecotic acid hydrazide. 1. Isonipecotic acid hydrazide. A solution of 5 g isonicotinic acid hydrazide in 75 ml 4% hydrochloric acid was subjected to hydrogenation at 18-20° and a pressure of 20-30 mm water column in presence of 0.2 g Adams platinum catalyst. After completion of the hydrogenation, the platinum was filtered off and the filtrate was evaporated in vacuo. The resulting viscous mass crystallized on trituration in presence of alcohol. Yield of isonipecotic acid hydrazide dihydrochloride 5.9 g (76%). Colorless crystals with m. p. 240-242°.**

2. Curtius reaction with isonipecotic acid hydrazide. A solution of 3.1 g sodium nitrite in 7 ml water was added dropwise with stirring to a solution of 5 g isonipecotic acid hydrazide dihydrochloride in 50 ml water (cooled to −5°). The reaction mass was left for an hour at about 0°. The solution was evaporated to one-sixth of its original volume. The precipitate was filtered off and boiled 4 hours with 50 ml ethyl alcohol. The alcohol was distilled off and the residue boiled 6 hours with 100 ml concentrated hydrochloric acid. The solution was evaporated to dryness. The residue was triturated in presence of anhydrous alcohol and recrystallized from alcohol. Yield of 4-aminopiperidine dihydrochloride 1.4 g (35%). Colorless crystals, m. p. 331-332°.

C. By the Schmidt reaction. 1. Isonipecotic acid hydrochloride. 15 g isonicotinic acid hydrochloride was hydrogenated in 225 ml 4% hydrochloric acid at 18-20° and a pressure of 20-30 cm water column in presence of 0.4 g Adams platinum catalyst. After completion of hydrogenation, the platinum was filtered off and the filtrate was evaporated to give 15.5 g isonipecotic acid hydrochloride (quantitative yield).

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*According to the literature [2] 4-aminopiperidine dihydrochloride has m. p. 332-335°.

**According to the literature [8], isonipecotic acid hydrazide dihydrochloride has m. p. 242-244°.

Colorless prisms; readily soluble in water and hot alcohol, insoluble in ether, chloroform, acetone and benzene. M. p. 299° (decomp.).*

Found %: C 43.55, 43.44; H 7.26, 7.09; Cl' 21.43, 21.25. $C_6H_{11}O_2N \cdot HCl$. Calculated %: C 43.50; H 7.25; Cl' 21.43.

2. Schmidt reaction with sodium azide. In the course of two hours 15.6 g sodium azide was added portionwise at 40° to a mixture (also heated to 40°) of 33.1 g isonipecotic acid hydrochloride, 100 ml anhydrous benzene and 80 ml concentrated sulfuric acid. The reaction mass was stirred 4 hours at 40°, and then 2-3 hours at the boil until nitrogen ceased to come off. It was treated with 40% sodium hydroxide solution until alkaline to phenolphthalein. The benzene layer was then separated. The aqueous alkaline solution was extracted with chloroform. The combined chloroform and benzene solutions were extracted with 15% hydrochloric acid and the acid extract was evaporated to dryness. The residue was triturated with anhydrous alcohol and 23 g (66%) 4-aminopiperidine dihydrochloride was obtained.

Colorless crystals, readily soluble in water and insoluble in common organic solvents. M. p. 332-334°.

Found %: C 34.62, 34.47; H 8.13, 8.23. $C_5H_{12}N_2 \cdot 2HCl$. Calculated %: C 34.68; H 8.09.

3. Schmidt reaction with hydrazoic acid. 25 ml of benzene solution of hydrazoic acid (containing 1.4 g N_3H) was added to a mixture (heated to 40°) of 8.95 g isonipecotic acid hydrochloride, 100 ml anhydrous benzene and 17.9 ml concentrated sulfuric acid. The temperature rose to 80° and the reaction was performed at 80° until nitrogen ceased to come off (about 2.5 hr). The reaction mass was thereupon cooled to 40° and a further 26 ml of benzene solution of hydrazoic acid (containing 1.43 g of the acid) was added. The temperature again gradually rose to 80° and the reaction was carried out at 80° again for about 2.5 hr until nitrogen ceased to be evolved. 4-Aminopiperidine dihydrochloride was isolated as in the preceding experiment. Yield 5.8 g (62%). Colorless crystals, m. p. 332-334°.

1-Formylisonipecotic acid. A mixture of 44 g isonipecotic acid hydrochloride, 18 g sodium formate and 150 ml formic acid was boiled 3 hours. The formic acid was distilled off in vacuo together with the water of reaction. Complete removal of the water was effected by treatment of the residue with benzene and redistillation in vacuo. After addition of 200 ml formic acid, the reaction mass was boiled for a further 4 hr. The process of distillation and boiling with a fresh portion of formic acid was again repeated. After distillation in vacuo the residue was dissolved in 200 ml water, made acid to Congo with hydrochloric acid, and extracted with chloroform. The extract was dried with sodium sulfate. Removal of the chloroform left 18.5 g (44%) of 1-formylisonipecotic acid.

Colorless crystals. Readily soluble in benzene and chloroform, poorly soluble in alcohol and acetone, insoluble in ether and water; m. p. 136-138°.

Found %: C 53.25, 53.12; H 7.19, 7.13; N 8.71, 8.86. $C_7H_{11}O_3N$. Calculated %: C 53.50; H 7.00; N 8.92.

1-Formyl-4-formylaminopiperidine. A mixture of 12.5 g 4-aminopiperidine dihydrochloride, 9.85 g sodium formate and 100 ml formamide was boiled 7 hr. The excess of formamide was distilled off in vacuo. The residue was treated with 50% potassium carbonate solution and extracted with chloroform. The chloroform solution was dried over potassium carbonate and the chloroform was distilled off. The residue was distilled in vacuo and a fraction with b. p. 195° (0.2 mm) was collected. The substance crystallized on rubbing. Yield 7 g (62.5%) 1-formyl-4-formylaminopiperidine.

Colorless crystals, readily soluble in chloroform, alcohols and acetone, insoluble in water, ether, benzene, toluene and ligroine; m. p. 77-79°.

Found %: C 53.88, 53.76; H 7.36, 7.64; N 17.60. $C_7H_{12}O_2N_2$. Calculated %: C 53.85; H 7.69; N 17.95.

SUMMARY

1. A comparative study was made of three undescribed variants of the preparation of 4-aminopiperidine using the reactions of Curtius, Hofmann and Schmidt.

*Literature [7]: m. p. 297-298° (decomp.).

2. A preparative method for the synthesis of 4-aminopiperidine from isonicotinic acid in two steps was developed. Over-all yield 66%.

3. Catalytic reduction of 4-aminopyridine to 4-aminopiperidine was effected.

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THE GLYCOSIDIC ALKALOID OF THE PLANT SOLANUM MEGAPARCUM KOIDZ

(LARGE-FRUITED NIGHTSHADE)

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Some of the newest modern sources of steroids are various varieties of nightshades containing glycosidic alkaloids with a steroid structure.

In the present paper we communicate the results of work on the chemical nature of one variety of nightshade, namely the large-fruited nightshade (Solanum megacarpum Koidz.). In its natural state this plant grows in river valleys, in thickets of bushes, in marshy meadows in Ukraine, Sakhalin, the Kurile islands and Japan. It is a dwarf shrub from the botanical section of the Dulcamara (Dun) Bitter and from the cycle of Dulcamara Pojark. For our work the plants were cultivated by the All-Union Institute of Medicinal and Aromatic Herbs (VILAR) under the conditions of the Moscow region. Seed material was obtained from the Botanical Institute of the Academy of Sciences of the USSR.

We collected the leaves and the tips of the young shoots during the period from the start of flowering to the start of ripening of the fruit.

The glycosidic alkaloids were extracted mainly by the method of Kuhn [1]. An alkaloid with the composition $C_{49}H_{81}O_{20}N$ with m. p. 260° was isolated. The quantity of substance was roughly 0.8% of the weight of raw material. Its properties show it to be different from any previously known glycosidic alkaloids. We therefore propose to name it "megacarpine." It forms a sulfate with m. p. 218-219° which is sparingly soluble in water. It was subjected to hydrolytic cleavage in dilute methanol in presence of hydrochloric acid. In this manner we obtained the hydrochloride of an alkaloid with the composition $C_{27}H_{45}O_2N \cdot HCl \cdot 0.5H_2O$, m. p. 298-299°. From the latter a base (aglucone) with the composition $C_{27}H_{45}O_2N \cdot H_2O$ with m. p. 206-208° was obtained. The elemental composition and melting point of the latter are similar to those of tomatidine [2]. They were shown to be different substances, however, by the sharp depression of melting point of a mixture of the two substances and by the difference in specific rotation. The molecule of the new aglucone does not contain a double bond since it does not give the Alberti reaction [3] and does not titrate with dibromopyridine sulfate [4]. The properties of the new aglucone show it to be different from any of the hitherto known aglucones, and we therefore propose to name it "megacarpidine." We determined the nature of the sugars formed on hydrolysis of megacarpine by paper chromatography. Glucose, galactose and xylose were detected. The qualitative composition of the sugars is thus the same as in tomatine and demissine [2, 5]. On the basis of the elemental composition of megacarpine and its aglucone, we can conclude that 4 molecules of simple sugars are present in megacarpine. From this it would follow that 2 molecules of one of the detected sugars must be present per molecule of megacarpine. According to calculations, the over-all specific rotation of a mixture comprising 1 mole glucose, 1 mole galactose and 2 moles xylose is +42.75°. For a mixture of the same sugars with 2 moles glucose the specific rotation would be +51.02°; for a mixture with 2 moles galactose it would be +58.12°. We found a value of +43.06° for the specific rotation of the total sugars obtained on hydrolysis of megacarpine, i.e., close to the value calculated for a mixture of sugars comprising 2 moles xylose, 1 mole galactose and 1 mole glucose.

In the light of the facts we suggest that megacarpine is dihydrosolasodine [6]. We are now making a study of the nature of megacarpidine.

EXPERIMENTAL

Isolation of the glycosidic alkaloid megacarpine. 900 g dried plant material was extracted with 5% acetic acid 3 times, each time with 18 liters, at 20°. The acetic acid extracts were made alkaline with ammonia to phenolphthalein and then heated to 70°. The resulting precipitates were separated from mother liquor on the next day by centrifuging. The dried precipitates were subjected to exhaustive extraction with methanol in presence of ammonia. Removal of the solvent left a dry, green residue. This was recrystallized from 50% alcohol to give 7.5 g of crystals. These were purified by two recrystallizations from 50% alcohol. After drying at 100° (3 mm) over P_2O_5 the compound had m. p. 259-260° (decomp.); $[\alpha]_D -61.6°$ (c 1.7, pyridine). On further drying at 100° (0.001 mm) the substance lost a further 6.8 % water.

Found %: 54.49; H 8.16; N 1.23. $C_{49}H_{81}O_{20}N$. Calculated %: C 54.66; H 8.34; N 1.34.

On standing in the air the glycosidic alkaloid again took up the water that it had lost on drying in high vacuum, in quantity corresponding to 4 moles H_2O per mole megacarpine. When an attempt was made to dissolve megacarpine in 2% H_2SO_4, the sulfate came down. It was recrystallized from 40% alcohol as white microcrystals with m. p. 218-219° (decomp.).

Hydrolysis of megacarpine. 2 g of megacarpine was boiled for 3 hours with a mixture of 100 ml 10% hydrochloric acid and 100 ml alcohol. The main bulk of alcohol was then distilled off in vacuo, and hot water was then added to the residue to make up the original volume. 0.8 g of the hydrochloride of the aglucone was obtained and was recrystallized from 75% methanol in the form of fine needles, m. p. 298-299° (decomp.). The substance was analyzed after drying at 100° (2 mm) over P_2O_5:

Found %: C 70.48; H 10.29; N 3.00. $C_{27}H_{45}O_2N \cdot HCl \cdot 0.5H_2O$. Calculated %: C 70.36; H 10.06; N 3.04.

The hydrochloride of the aglucone last 1.81% water on drying in high vacuum (0.001 mm) at 100°. Calculated for 0.5 mole H_2O: 1.95%.

On standing in the air the hydrochloride of the aglucone quickly took up the moisture which it had lost when dried in high vacuum.

0.6 g aglucone hydrochloride was dissolved in 26 ml 75% methanol by boiling. To the hot solution was added an excess of concentrated ammonia. 0.53 g crystalline megacarpidine was obtained; after recrystallization from 100 ml 80% methanol and drying at 100° (2 mm) over P_2O_5 it had m. p. 206-208°; $[\alpha]_D -54.3°$ (c 0.5, methanol).

Found %: C 75.04; H 10.80; N 3.18. $C_{27}H_{45}O_2N \cdot H_2O$. Calculated %: C 74.76; H 10.96; N 3.23.

Megacarpidine loses 4.16% water when dried in high vacuum at 100° (0.001 mm). Calculated for 1 mole H_2O: 4.16. It again takes up one mole water from the atmosphere on standing.

Megacarpidine picrolonate was obtained on mixing alcoholic solutions of megacarpidine and picrolonic acid: white needles (from alcohol), m. p. 218-219°. Megacarpidine picrate is readily soluble in alcohol and is prepared by evaporting an alcoholic solution of a mixture of megacarpidine and picric acid and subsequent recrystallization of the dry residue from 40% alcohol. M. p. 152-154° (with softening at about 142°).

Determination of sugars in the product of hydrolysis of megacarpine. 0.16 g megacarpine was boiled with 5 ml alcohol and 5 ml 10% H_2SO_4 for 3.5 hr. The alcohol was then taken off in vacuo and 4 ml water was added. The mixture was heated on a boiling bath and left until the next day. The precipitated megacarpidine sulfate was filtered off and the filtrate neutralized with $BaCO_3$. The filtrate from the resulting precipitate was concentrated to 3 ml. This solution was used in determination of sugars by paper chromatography with indicators: glucose, galactose, rhamnose and xylose. Solvents: mixture of n-butyl alcohol, pyridine and water (3 : 2 : 1.5) [7]. Ascending chromatography was effected in the course of 15 hours. The traces were developed with a solution of aniline hydrophthalate in n-butyl alcohol [8]. Three traces were obtained with R_f: 0.49, 0.40 and 0.35, corresponding to xylose, glucose and galactose.

For quantitative determination of the sugars, 1.4965 g megacarpine (containing 4 moles H_2O) was heated with 80 ml 5% H_2SO_4 4 hours. The resulting megacarpidine sulfate was filtered off and washed with hot water. The acid filtrate and the wash liquors were neutralized with $BaCO_3$ while being heated on a boiling water bath.

After standing, the precipitate was filtered and thoroughly washed with water. The nearly colorless filtrate, together with the wash liquors, was evaporated in vacuo and made up to 24.5 ml in a pycnometer together with 1 drop 10% NH_3 solution. α_D +3.23°, (l 2), $[\alpha]_D$ +43.06° (on the assumption that 1.4965 g megacarpine gives 0.919 g sugars). This is close to the calculated value of $[\alpha]_D$ for a mixture of alcohols comprising 2 moles xylose, 1 mole glucose and 1 mole galactose (+42.75°).

SUMMARY

1. A new glycosidic alkaloid – megacarpine, composition $C_{49}H_{81}O_{20}N$) – was isolated from the leaves and young shoots of Solanum megacarpum Koidz. (large-fruited nightshade).

2. Hydrolytic cleavage in presence of mineral acids yielded a new aglucone – megacarpidine, composition $C_{27}H_{45}O_2N \cdot H_2O$.

3. It was established that acid hydrolysis causes cleavage of the megacarpine molecule with formation of 1 mole megacarpidine, 1 mole glucose, 1 mole galactose and 2 moles xylose.

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XXXV. REACTION OF 1,1-DIFLUOROTETRACHLOROCYCLOPENTADIENE WITH SOME UNSATURATED COMPOUNDS

S. D. Volodkovich, N. N. Mel'nikov, A. F. Plate and M. A. Prianishnikova

In recent years the literature has described a fairly large number of polycyclic compounds which were obtained by condensation of hexachlorocyclopentadiene with various unsaturated compounds [1-5]. Some compounds of this type are now used fairly widely in agriculture for control of harmful plants and also as raw material for production of nonflammable plastic masses [6]. Reports have recently appeared about the synthesis of a series of polychloropolyfluoro derivatives of cyclic hydrocarbons, two of which possess appreciable insecticidal activity [7]. The only members of this group whose preparation has hitherto been described in the literature are products of condensation of 1,1-difluorotetrachlorocyclopentadiene with cyclopentadiene, methylcyclopentadiene, maleic anhydride, benzoquinone, styrene, p-chlorostyrene and acrylic acid [7, 8].

We are studying the mechanism of the action on insects of chlorine-containing insecticides of the type of Aldrin, Dildrin and their analogs and are compiling data on the dependence of the insecticidal action of this group of compounds on structure. In this connection it was of interest to synthesize previously undescribed fluorine-containing analogs of Aldrin and to study their insecticidal activity.

In the first instance we synthesized 1,2,3,4-tetrachloro-10,10-difluoro-1,4,5,8-diendomethylene-1,4,4a-5,8,8a-hexahydronaphthalene and 1,2,3,4-tetrachloro-10,10-difluoro-1,4,5,8-diendomethylene-1,4,4a,5,6,7,8-8a-octahydronaphthalene by interaction of 1,1-difluorotetrachlorocyclopentadiene with bicyclo-[2,2,1]-2,5-heptadiene and bicyclo-[2,2,1]-2-heptene. These compounds are the nearest analogs of Aldrin, and considerable interest is attached to their study. In addition we synthesized the adducts of 1,1-difluorotetrachlorocyclopentadiene with cyclopentene, 5-amylbicyclo-[2,2,1]-heptene-2,5-methylbicyclo-[2,2,1]-2-heptene-5-carboxylic acid, acrylonitrile, and esters of maleic acid. The compounds that we synthesized and their properties are listed in the Table.

The reaction of 1,1-difluorotetrachlorocyclopentadiene with the above unsaturated compounds goes relatively easily when the mixture of reactants is heated for a short period on a water bath. The yields of adducts of 1,1-difluorotetrachlorocyclopentadiene with the different unsaturated compounds are small, however, due to 1,1-difluorotetrachlorocyclopentadiene polymerizing fairly easily and forming an inert dimer.

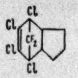
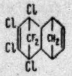
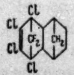
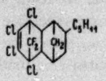
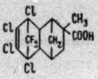
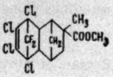
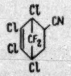
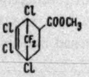
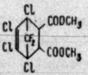
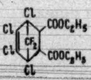
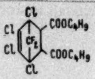
Nearly all of the compounds that we synthesized were found to have poor insecticidal activity in tests carried out by E. F. Granin. An exception is 1,2,3,4-tetrachloro-10,10-difluoro-1,4,5,8-diendomethylene-1,4,4a,5,8,8a-hexahydronaphthalene (difluoroaldrin), which is slightly inferior to chlorindan in activity.

EXPERIMENTAL

Starting substances. Cyclopentene was prepared by dehydration of cyclopentanol over alumina at 400°; homologs and derivatives of bicyclo-2,2,1-heptene were synthesized by the diene synthesis from cyclopentadiene and the corresponding olefins [9]. Bicyclo-[2.2,1]-2,5-heptadiene was obtained by condensation of cyclopentadiene with acetylene at elevated temperature and pressure [10]. Esters of maleic acid were prepared from the corresponding alcohols and maleic anhydride in presence of catalytic quantities of sulfuric acid.

1,1-Difluorotetrachlorocyclopentadiene was obtained by fluorination of octachlorocyclopentene with

Properties of Products of Condensation of 1,1-Difluorotetrachlorocyclopentadiene with Some

Formula	Yield (in %)	Boiling point (pressure in mm)	Melting point	n_D^{20}	d_4^{20}
	25	143—145° (19)	43—44°	—	—
	60	163—165 (20)	38—39	—	—
	81	—	47—48	—	—
	46	182—183 (5)	—	1.5080	1.3158
	71	—	205—6	—	—
	48	186—187 (8)	—	1.5210	1.4906
	65	135—138 (12)	—	1.5118	1.6215
	44	130—132 (10)	—	1.4970	1.5680
	26	155—157 (10)	75—76	—	—
	44	165—168 (7)	—	1.4990	1.5054
	23	187—189 (5)	—	1.4825	1.3440

MR		Analysis (%)			
		C		H	
calculated	found	calculated	found	calculated	found
—	—	38.96	38.84, 38.63	2.61	2.96, 2.91
—	—	43.40	43.88, 43.65	2.43	3.01, 3.34
—	—	43.14	42.56, 43.38	3.02	3.41, 3.51
90.9	91.5	50.49	49.93, 49.55	4.95	4.97, 4.88
—	—	42.85	43.13, 43.36	3.06	3.49, 3.52
83.11	82.8	44.33	43.63, 44.13	3.44	3.65, 4.09
53.62	54.21	32.76	33.54, 33.75	1.02	1.76, 1.99
60.00	60.60	33.12	32.40, 32.77	1.84	2.43, 2.48
—	—	34.37	34.20, 34.34	2.08	2.57, 2.48
79.93	80.35	37.86	37.40, 37.17	2.91	2.64, 2.90
98.40	99.23	43.59	43.08, 43.16	4.27	4.54, 4.60

antimony fluoride in presence of antimony pentachloride at 160-170°. The resulting difluorohexachlorocyclopentene was dechlorinated with zinc dust in sulfuric acid [7, 8]. The 1,1-difluorotetrachlorocyclopentadiene used for the syntheses had b. p. 70-71° (20 mm), d^{20}_4 1.7382, $n^{20}D$ 1.4990.

Condensation of 1,1-difluorotetrachlorocyclopentadiene with unsaturated compounds. An equimolar mixture of the reactants was refluxed with good stirring for 1-6 hours on a water bath. At the end of the reaction the mixture was fractionated in vacuo and analyzed. In all cases fractionation gave fairly large quantities of the original unsaturated compound and of the dimer of 1,1-difluorotetrachlorocyclopentadiene. Increased yields of adduct and purer products are obtained by conducting the reaction with excess of unsaturated compound. In this case the quantity of dimer of difluorotetrachlorocyclopentadiene is slightly reduced. For the preparation of "difluoroaldrin," for example, we took a threefold excess of the starting hydrocarbon. The synthesized compounds and their properties are listed in the Table.

SUMMARY

The condensation of 1,1-difluorotetrachlorocyclopentadiene with various unsaturated compounds was studied. It was shown that this reaction goes in a manner entirely similar to the condensation of hexachlorocyclopentadiene but with somewhat greater facility. A series of fluorochloro derivatives of polycyclic hydrocarbons not previously described in the literature were synthesized.

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INVESTIGATION OF ACONITE ALKALOIDS

XIII. THE ALKALOIDS OF ACONITUM ROTUNDIFOLIUM KAR. AND KIR. AND ACONITUM NEMORUM M. POP. [1]

T. F. Platonova, A. D. Kuzovkov and P. S. Massagetov

The round-leaved aconite (Aconitum rotundifolium Kar. et Kir.) is a small perennial with two small tubers and pale-lilac flowers. For the purpose of isolation of the alkaloids, the above-ground portions were collected during the flowering period (August-September) in Central Tien Shan. The dried plant contained about 0.15% of a mixture of alkaloids in which four bases were detected by paper chromatography. An alkaloid $C_{27}H_{31}O_6N$ and another with the composition $C_{26}H_{34}O_2N_2$ were isolated by chromatography on alumina.

The forest aconite (Aconitum nemorum M. Pop.) is a perennial herbaceous plant with blue flowers and a chain of intergrowing tubers. Whole plants were collected in August during the flowering period in Tien Shan in the region of Lake Son-Kul. The dried plant contained 0.2% of a mixture of alkaloids. Two bases were detected by paper chromatography which were identified as talatisamine [2] and its monoacetyl derivative; the last substance was obtained [3] by acetylation of talatisamine but it had not previously been found in plants.

EXPERIMENTAL

Isolation of Alkaloids from Aconitum rotundifolium

8 kg air-dry plant was wetted with 4 liters of 5% sodium carbonate solution and exhaustively extracted with dichloroethane. The bases were extracted from the extract with 5% sulfuric acid. Alkalization of the sulfuric acid solution with sodium carbonate led to deposition of 5.5 g of crystals (fraction a). Extraction of the mother liquor with chloroform gave 8 g of noncrystallizing mixture of alkaloids (fraction b). Paper chromatography revealed the presence in fraction a of four bases (R_f 0.85, 0.78, 0.54 and 0.35). The same bases are also found in fraction b. 5.5 g of the mixture of bases (a) was dissolved in 55 ml chloroform and chromatogrammed on 120 g Al_2O_3. Elution with chloroform gave 0.1 g of base with R_f 0.82 which melted, after 2 recrystallizations from acetone, at 251.5-252°.

Found %: C 69.21, 69.37; H 6.71, 6.58; N 2.96, 2.75; NCH_3 2.68; OCH_3 none. $C_{27}H_{31}O_6N$. Calculated %: C 69.66; H 6.71; N 3.01; NCH_3 6.23.

The hydrochloride crystallizes from a mixture of alcohol and ether; m. p. 306°.

Elution with a mixture of chloroform and 1% methanol gave 0.2 g of a crystalline mixture of bases which was resolved by treatment with hot acetone. The insoluble portion was a mixture of 3 substances (R_f 0.75, 0.54, 0.16). From the dissolved portion was obtained 0.05 g of a base with R_f 0.56, m. p. 173-174° (from acetone).

Found %: C 77.08, 77.87; H 8.42, 8.70; N 6.93. M 465 (Rast method). $C_{26}H_{34}O_2N_2$. Calculated %: C 76.81; H 8.43; N 6.89. M 406.6.

Separation of Alkaloids from Aconitum nemorum

Alkaloids were extracted from 6 kg air-dry plant by extraction with dichloroethane as described above.

The sulfuric acid extract was made alkaline with sodium carbonate and extracted with chloroform. There was obtained 12 g of a noncrystalline mixture of bases (R_f 0.36, 0.46, 0.74) which was dissolved in 250 ml chloroform and chromatogrammed on 250 g alumina. Elution with chloroform gave 1.6 g of an oily product (R_f 0.45) from which 0.6 g monoacetyltalatisamine (m. p. 95-97° from hexane) was isolated by treatment with hexane; R_f 0.45. No depression of melting point was observed in admixture with the monoacetyl derivative prepared from talatisamine. Elution with a mixture of chloroform and 10% methanol gave 3.2 g talatisamine m. p. 142-143.5°, R_f 0.36. 1-Butanol saturated with 5% acetic acid was used as the stationary phase in paper chromatography; development was effected with Dragendorf's reagent.

SUMMARY

1. Alkaloids $C_{27}H_{31}O_6N$, m. p. 251.5-252° and $C_{26}H_{34}O_2N_2$ with m. p. 173-174° were isolated from Aconitum rotundifolium Kar. et Kir.

2. Talatisamine and monoacetyltalatisamine were isolated from Aconitum nemorum.

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ALKALOIDS OF THE CHENOPODIACEAE (GOOSEFOOT)

ANABASIS JAXARTICA AND ARTHROPHYTUM LEPTOCLADUM

T. F. Platonova, A. D. Kuzovkov and P. S. Massagetov

Anabasis jaxatica (Bge.) Benth, the Syr-Dar'e anabasis, is a small (20-30 cm tall) perennial which is plentiful in the solonetz plains bordering on the River Syr-Dar'e. The investigated material consisted of year-old shoots collected in the early stage of growth of the plant (before flowering) in the Dzhambui oblast of the Kazakh SSR. The dry plant contained 0.16% of a mixture of alkaloids in which four bases were detected by paper chromatography (R_f 0.80, 0.41, 0.33, 0.17). Two bases could be isolated on the basis of their differing basicities: No. 1 (R_f 0.33) and No. 2 (R_f0.41). Compounds with R_f 0.80 and 0.17 give weak traces on the chromatogram and are evidently present in insignificant quantity in the plant. The composition of base No. 1 corresponds to $C_9H_{13}ON$; it melts at 133-134.5°, dissolves in water,gives a violet color with ferric chloride solution. Its infrared spectrum contains absorption bands at 3.0 μ (weak, NH), 3.8 μ (doublet, zwitterion), 6.2 μ (doublet, conjugated bonds). It forms an N-acetyl derivative with acetyl chloride, indicating the presence of secondary nitrogen. Oxidation of the O-methyl derivative of base No. 1 gave p-methoxybenzoic acid. The composition and properties of base No. 1 and the constants of its salts are similar to those of N-methyl-4-hydroxy-β-phenylethylamine [1] (Table 1).

The above data provide sufficient evidence of the identity of these substances. It may be noted that N-methyl-4-hydroxy-β-phenylethylamine has not hitherto been found in plants, although its N-methyl derivative – gordenine [2] – has been known for a long time. Base No. 2, $C_{10}H_{15}ON$, differs from No. 1 in containing an additional CH_2 group. The compound melts at 166-169°. Zwitterion absorption bands are present in the infrared spectrum, very close to the bands of No. 1 (3.7, 3.8 μ) as well as conjugated double-bond bands (6.2 μ). This compound is new, and we propose the name of "jaxartininex."

Arthrophytum leptocladum M. Pop. (thin-stemmed haloxylon). The alkaloids of this plant were previously investigated by N. K. Iurashevskii [3] who isolated dipterine, leptocladine and N-methyl-β-phenylethylamine. The sample of the plant that we studied (year-old green shoots in the flowering period) was collected in the Surkhan-Dar'in oblast of the Uzbek SSR. It was extremely rich in alkaloids (3.7% content of mixture of bases). In addition to dipterine and leptocladine we were able to isolate a base $C_{12}H_{14}N_2$ with m. p. 216-218°. The latter contains one NCH_3 group. One of the two nitrogen atoms possesses marked basic properties: with excess of hydrochloric acid the base forms a monohydrochloride $C_{12}H_{14}N_2 \cdot HCl$. The infrared spectrum contains an absorption band of the associated NH group (3.2 μ). The ultraviolet absorption spectrum is similar to that of indole with λ_{max} 228, 280 mμ (log ε 4.28, 3.90).

On the basis of the above data, and taking into account the similarity between the constants of our base and its salts and those of 3-methyl-1,2,3,4-tetrahydro-β-carboline [4] (see Table 2), we can regard these two compounds as identical.

EXPERIMENTAL

Alkaloids of Anabasis jaxartica. Eleven kg dry, pulverized plant was extracted by the usual method [5]. From the ethereal extract was obtained 11.7 g (fraction a), and from the chloroform extract 5.9 g (fraction b) of noncrystalline total bases. Total content of alkaloids 0.16%. Paper chromatography in the system butanol – 5% acetic acid revealed the presence of four substances: R_f 0.80, 0.41, 0.33, 0.17. The compounds with R_f 0.8 and 0.17 give very weakly colored traces on the paper. The compound with R_f 0.33 was developed by iodine vapor and the others by Dragendorf reagent.

TABLE 1

Preparation number	Name of substance	N-Methyl-4-hydroxy-β-phenylethylamine	Base No. 1
1	Base { comp.	$C_9H_{13}ON$	$C_9H_{13}ON$
	m. p.	128-130°; 130°	133-134.5°
2	Hydrochloride, m. p.	146-147°; 148°	149-150.5°
3	Picrate, m. p.	149°	148-148.5°
4	Picrolonate, m. p.	234-235°	238°
5	Acid oxalate, m. p.	250°	251°

TABLE 2

Preparation number	Name of substance	3-Methyl-1,2,3,4-tetrahydro-β-carboline	Base
1	Base { comp.	$C_{12}H_{14}N_2$	$C_{12}H_{14}N_2$
	m. p.	216-217°	216-218°
2	Picrate, m. p.	197-198°	195-197°
3	Methoiodide, m. p.	265°	265 – 266°
4	Benzyl chloride, m. p.	165°	Contracts at 165° Melts at 202°

11.7 g bases (fraction a) was dissolved in 30 ml 1 N sulfuric acid. Fractional alkalization of the solution gave 10 fractions; extraction of bases from each fraction was effected with ether. The 5th and 6th fractions, after trituration in presence of acetone, gave 0.1 g of jaxarthinine; from the 9th and 10th fractions was obtained 0.55 g of base No. 1. 5.9 g of bases b was dissolved in 50 ml water, the solution was washed with ether and benzene and then evaporated to dryness. Trituration of the residue with acetone gave 0.4 g of base No. 1. All the mother liquors from treatment of fractions a and b were combined and the bases were distilled in vacuo (0.1 mm); from the fraction with b. p. 170-180° was isolated 0.6 g of base No. 1.

Base No. 1, m. p. 133-134.5° (from acetone), R_f 0.33; soluble in water, chloroform, ether, acetone, and methanol.

Found %: C 71.72, 71.54; H 8.68, 8.50; N 8.94, 9.28. M 185 (Rast's method). $C_9H_{13}ON$. Calculated %: C 71.53; H 8.67; N 9.27. M 152.

The hydrochloride was prepared by mixing alcoholic solutions of the base and hydrochloric acid; m. p. 149-150.5° (from alcohol-ether mixture).

Found %: Cl 18.81, 18.78. $C_9H_{13}ON \cdot HCl$. Calculated %: Cl 18.89.

Picrate, m. p. 148-148.5° (from alcohol). Picrolonate, m. p. 238° (decomp.). Acid oxalate, m. p. 251° (from alcohol). All of these salts were prepared by mixing alcoholic solutions of the base and the corresponding acid.

0.2 g base No. 1 and 5 ml acetyl chloride were boiled 2 hours. 0.1 g of N-acetate was obtained; m. p. 140-142° (from methanol). The zwitterion band and the 3 μ band (NH) were absent from the infrared spectrum, which contained a strong band at 3.1 μ (OH group) and which had a stronger 1613 cm^{-1} band in the 6.2 μ region (amide-carbonyl) than in the spectrum of base No. 1.

To a solution of 0.5 g base in 3 ml 10% NaOH was added 1 ml dimethyl sulfate; the mixture was heated one hour; after dilution to 20 ml with water, 3 g $KMnO_4$ was added portionwise in the course of 4 hours, at first at room temperature and later at 100°. The MnO_2 was filtered off and the filtrate acidified with hydrochloric acid and extracted with ether. 0.05 g acid was obtained with m. p. 184-185°; no depression of melting point in admixture with p-methoxybenozoic acid.

Jaxarthinine, m. p. 166-169° (from acetone), R_f 0.41; readily soluble in chloroform, less soluble in acetone.

Found %: C 72.85, 72.94; H 8.67, 8.83; N 8.54, 8.73. $C_{10}H_{15}ON$. Calculated %: C 72.70; H 9.15; N 8.47.

Alkaloids of Arthrophytum leptocladum. 16 kg dried plants was worked up as previously described. From the ethereal fraction was obtained 570 g (fraction a) and from the chloroform fraction 30 g (fraction b) of a noncrystalline mixture of bases. Alkaloid content 3.7%. Paper chromatography revealed the presence of substances with R_f 0.48, 0.53 and 0.60.

310 g of the mixture of bases (fraction a) was distilled at 8 mm to give the following fractions: 1st, to 195°, 15 g; 2nd, 195-205°, 144 g; 3rd, 206-230°, 46 g. Mixing of the 2nd fraction with ether (1:1) led to separation of 50 g dipterine, m. p. 88-90° (from ether). Similar treatment of the 3rd fraction led to deposition of a base (2.2 g) with m. p. 216-218° (from methanol). The ether was removed from the mother liquors of the 2nd and 3rd fractions, the residue was dissolved in acetone, and alcoholic hydrochloric acid was added. In this manner 31 g of leptocladine hydrochloride was obtained; m. p. 230-232°. Dipterine and leptocladine were identified by direct comparison with corresponding specimens of the bases and their salts.

260 g of the mixture of bases (a) was divided into 15 smaller fractions by fractional alkalization. From the 6th to 10th fractions was obtained leptocladine in the form of the hydrochloride (7.5 g); the 13th and 14th fractions yielded 9 g dipterine. The mother liquors from all of the fractions were combined and the bases with them were distilled at 8 mm in the ranges described above. From the 3rd fraction was isolated 0.7 g of base with m. p. 216-218° (from methanol); readily soluble in chloroform, less soluble in acetone, alcohol and ether.

Found %: C 77.34, 77.79; H 7.18, 7.63; N 15.04, 14.89; NCH_3 10.9. M 201(Rast method). $C_{12}H_{14}N_2$. Calculated %: C 77.40; H 7.57; N 15.03; NCH_3 15.59. M 186.

Hydrochloride, m. p. 245-247° (from a mixture of alcohol and ether).

Found %: C 65.07; H 6.82; Cl 16.00. $C_{12}H_{14}N_2 \cdot HCl$. Calculated %: C 65.01; H 6.82; Cl 15.99.

Picrate, m. p. 195-197° (from alcohol). The methoiodide was obtained by heating the base with methyl iodide in a sealed tube at 100° for 7 hours; m. p. 265-266° (from alcohol).

The benzyl chloride derivative was obtained by heating a solution of the base in benzene with benzyl chloride for 30 minutes. The compound turns yellow and contracts at 165° and melts at 202° (from a mixture of ether and alcohol).

SUMMARY

1. N-Methyl-4-hydroxy-β-phenylethylamine and a new alkaloid, jaxarthinine, $C_{10}H_{15}ON$ (m. p. 166-169°) were isolated from the plant Anabasis jaxartica of the family of the Chenopodiaceae (Goosefoot).

2. 3-Methyl-1,2,3,4-tetrahydro-β-carboline was isolated from Arthrophytum eptocladum, a plant of the same family.

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ALKALOIDS OF PLANTS OF THE FAMILY OF THE ASCLEPIADACEAE (MILKWEED)

I. ANTITOXICUM FUNEBRE (BOISS. ET KY.) POBED.

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Very little is known about the alkaloids of the plants of the milkweed family. Isolation of two alkaloids from Tilophora asthmatica Wigt & Arn. has been reported [1]: tilophorine $C_{24}H_{27}O_4N$ and tilophorinine $C_{23}H_{27}O_4N$. Nicotine has been found in Asclepias syriaca [2]. Up to 40 varieties of plants of this family are found in the USSR [3], but only two of these have been subjected to chemical investigation: Cynanchum acutum L. and Vincetoxicum sibiricum. No alkaloids were detected, however, in these plants [4].

In view of the great interest recently shown in the alkaloids of plants of the Apocynaceae family and the close botanical relationship between this family and that of the Asclepiadaceae, we decided to undertake a study of the alkaloids of the latter. Antitoxicum funebre (Boiss. et Ky.) Pobed. is a plant 40-70 cm high with straight single and sometimes branchy shoots, growing on dry stony slopes in screes and arid areas. The dried above-ground portions of the plant collected in Caucasia in June 1953 contained 0.26% of total alkaloids. Paper chromatography established the presence of substances with R_f 0.45 and 0.33. Chromatography of the total alkaloids on alumina led to isolation of a base $C_{23}H_{25}O_3N$ with m. p. 213-215°, R_f 0.45, containing 3 OCH_3 groups. The infrared spectrum of the base does not contain bands of lactamic carbonyls or of OH and NH groups. This is a new alkaloid, and we propose to call it antophine. Extremely small quantities of two other bases were also isolated and were characterized only by their melting points. One of them melts at 113-116°, then solidifies and again melts at 239°; R_f 0.42; the other has m. p. 225-226°, R_f 0.33.

EXPERIMENTAL

Two kg dry, pulverized above-ground portions of the plant were moistened with aqueous ammonia and extracted with dichloroethane. The material was worked up in the usual manner [5]. From the ethereal extract was obtained 4.9 g (fraction a) and from the chloroform extract 0.4 g (fraction b) of bases in the form of oil-containing crystals. Paper chromatography in the system butanol – 5% acetic acid led to detection of substances with R_f 0.45 and 0.33. On rubbing fraction a and a little acetone, 0.5 g of crystals was obtained; the same treatment of fraction b gave 0.05 g of crystals. Evaporation of the acetonic mother liquors gave a noncrystalline mixture of bases (fraction c). A solution of 0.55 g of the crystalline substance in 15 ml chloroform was passed through a column containing 20 g alumina. The alkaloids were eluted at first with chloroform and then with a mixture of chloroform and methanol (1, 2, 5 and 10% methanol). Ten fractions were obtained. From the 1st fraction was isolated 0.25 g antophine, but no pure substances were separated from the other fractions. 4.3 g of the mixture of bases (fraction c) was dissolved in 80 ml chloroform and the solution was passed through a column containing 150 g alumina. Elution was effected as described above. Fifteen fractions were obtained and were treated with acetone to give: 0.1 g antophine from the 1st fraction and 0.03 g of a base from the 9th fraction. The latter melted at 113-116°, then solidified and finally remelted at 239° (from a mixture of methanol and ether), R_f 0.42. This substance fluoresced strongly in the ultraviolet. From the 13th fraction was isolated 0.03 g of a base with m. p. 225-226° (from methanol), R_f 0.33. Antophine is poorly soluble in alcohol and acetone, readily soluble in chloroform; m. p. 213-215° (from acetone), R_f 0.45.

Found %: C 76.14, 75.85; H 7.00, 7.18; N 4.16, 3.98; OCH_3 23.27. $C_{23}H_{25}O_3N$. Calculated %: C 76.01; H 6.93; N 3.85; 3 OCH_3 25.59.

SUMMARY

A new alkaloid, antophine, with the composition $C_{23}H_{25}O_3N$ and two uncharacterized bases were isolated from Antitoxicum funebre (Boiss. et Ky.) Pobed. of the family of the Asclepiadaceae.

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SPECTROPHOTOMETRY OF BIURET COMPLEXES AS A METHOD OF INVESTIGATION OF POLYPEPTIDES AND PROTEINS

XIX. SOME DOUBLE DECOMPOSITION REACTIONS OF COPPER-BIURET COMPLEXES

M. I. Plekhan

In earlier spectrophotometric studies of copper-biuret complexes we arrived at the conclusion that the chromophoric properties of these compounds are associated with coordinated bonds and that consequently a difference in the character of the absorption reflects a difference in the composition of the inner shell of the coordination sphere of the complexes. On the basis of these considerations we proposed a classification of copper-biuret complexes that differed fundamentally from the classification advanced in 1916 by Kober and Haw [2]. We may recall that the latter attributed the chromophoric porperties not to coordination bonds but to the copper atom itself in one stage or other of its hydration. The classification of Kober and Haw postulated the existence in general of only three complexes which characterize the three hydration stages of the copper atom, and in their work they attempted to show that the colors of the complexes can be arranged in three – and only three – classes and that the absorption spectra of a class are substantially identical [2]. The latter assertion of Kober and Haw was based on their numerous but technically inaccurate measurements which failed to differentiate between the fine distinctions in the character of absorption of the complexes. Thus, for example, according to the data of Kober and Haw the red copper-biuret complexes of biuret and a tetrapeptide have the same absorption character. Our measurements showed, however, that this is not true, the maximum of the biuret complex being at 535 mμ and that of the tetrapeptide complex at 520 mμ. The molecular intensity of absorption of the biuret complex is one-quarter of that of the tetrapeptide complex. In our investigations we have adduced other examples that show the fallacy in the ideas of Kober and Haw.

In the present work we have also confirmed the existence of a direct relation between the properties of the complex and the composition of the coordination bonds. Here we examined the relative stabilities of copper-biuret complex in some double decomposition reactions.

1. Wavelength of absorption maximum as a criterion of the relative stability of a copper-biuret complex. In preceding communications we had already drawn attention to the differing activitives of formation of biuret complexes which are reflected in the ability of one substance to displace another from a complex [3]. This effect undoubtedly involves not only the activity of formation but also the strength of the coordinative bonds of the complex. In the present work we tried to establish a connection between the character of the absorption and the relative stability of copper-biuret complexes in the above type of reaction starting from the assumption that the most stable complexes must possess maximum absorption of the shortest waves.

An experiment was therefore designed to examine spectrophotometrically the stability of copper-biuret complexes. This involved the addition to their solutions of substances possessing a maximum at a shorter wavelength. It was of particular interest to clarify the behavior under these conditions of completed red complexes in order to establish whether any differences arise in stability within one group of complexes.

The following facts emerged from the experiments: a) addition of a tetrapeptide (glycine) to a light-pink solution of copper-biuret complex (0.154%) very soon led to development of a deep-red color (see Experimental for details). Spectrophotometric examination of the solutions showed that the character of the absorption undergoes a profound change. Solution I of the biuret complex possessed an absorption maximum at 535 mμ, $\epsilon_{\max}$ 0.256 (Fig. 1, I). Twenty minutes after the addition of the tetrapeptide the maximum moved into the

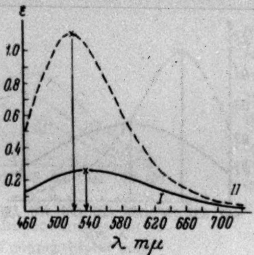


Fig. 1. Spectrophotometric curves. I) Solution of copper-biuret complex (0.154%); II) the same, 20 minutes after addition of triglycylglycine.

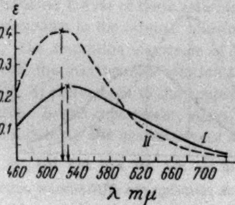
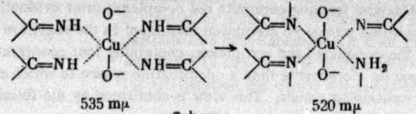


Fig. 2. Spectrophotometric curves. I) Solution of copper-biuret complex of leucylglycylasparagine (0.015%); II) ditto 20 minutes after addition of triglycylglycine.

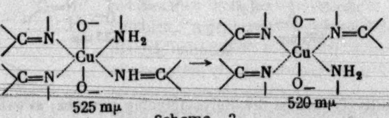
wavelength of 520 mμ and the intensity of the maximum of absorption rose to ϵ_{max} 1.1. The resulting solution II corresponds to a solution of the copper-biuret complex of the tetrapeptide (Fig. 1, II). The reverse process does not occur, i.e., addition of biuret to a solution of the complex of the tetrapeptide does not result in displacement of the tetrapeptide. Consequently, the coordination bonds of the biuret complex are weaker than the coordination bonds of the tetrapeptide complex. It should be pointed out that the wavelength of maximum absorption of the biuret complex is higher than that of the maximum of the tetrapeptide complex.

The process of displacement in the present case can be represented by the arbitrary scheme.*



Scheme 1

b) To the red solution I (0.105%) of the copper-biuret complex of leucylglycylasparagine was added the tetrapeptide; after 20 minutes solution II is formed; this corresponds to the copper-biuret complex of the tetrapeptide. The maximum of the original solution I (see Fig. 2, I) is at 525 mμ, ϵ_{max} 0.233. The maximum of solution II (Fig. 2, II) is at 520 mμ, ϵ_{max} 0.403. The coordination sphere of the leucine-glycine-asparagine complex is less stable than that of the tetrapeptide and is characterized by absorption of longer waves. The displacement process is represented by scheme 2.



Scheme 2

It is interesting to note that the difference in composition of the coordination bonds of these complexes consists in the fourth coordination bond of leucylglycylasparagine being formed by an amide group while in the

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* We previously gave the detailed structural formulas of the complexes [1]; in the present case we limit ourselves to depicting only the inner coordination sphere of the complex. We do not feel that a final explanation has been given on the problem of the nature of the bonds between the copper atom and the enolic hydroxyls.

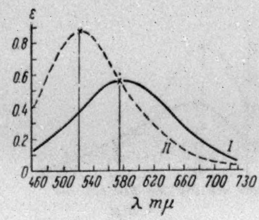


Fig. 3. Spectrophotometric curves. I) Solution of copper-biuret complex of diglycylglycine (0.126%); II) ditto 20 minutes after addition of triglycylglycine.

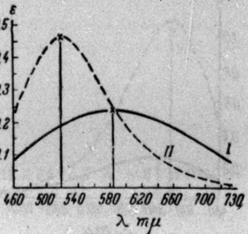
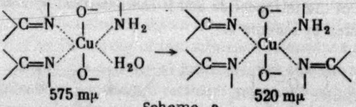


Fig. 4. Spectrophotometric curves. I) Solution of copper-biuret complex of leucylglycyltryptophan (0.13%); II) ditto 20 minutes after addition of triglycylglycine.

triglycylglycine complex it is a peptide group. Consequently the exchange of one group by the other causes the absorption maximum to be shifted by 5 mμ. In the preceding experiment (scheme 1) the replacement of then three amide groups in the coordination sphere of the complex (biuret) by three peptide groups led to a 15 mμ shift in the absorption maximum, i.e., a 5 mμ shift of maximum is likewise associated with each newly formed coordination bond with a peptide group. We previously put forward the hypothesis [1] that light absorption by copper-biuret complexes presumably bears a certain additive character and is governed by the sum of the absorptions of the individual coordinative bonds. This hypothesis is supported by the experiments described above.

If it is true that the position of the absorption maximum can serve as a criterion of the relative stability of a biuret complex, then substances forming complete red complexes must evidently always decompose the incomplete violet complexes which possess an absorption maximum in the region of longer wavelengths. The inner coordination sphere of the completed red complexes, containing four coordination bonds with nitrogen-containing groups, must always be more stable than a coordination sphere in which one or two coordination bonds are formed by oxygen-containing groups. This view is confirmed by the following experiments.

c) Tetrapeptide was added to the violet solution I of the copper complex of diglycylglycine (0.126%). The color changed very quickly and red solution II was formed. Figure 3 (curve I) shows that solution I had maximum absorption at 575 mμ and ϵ_{max} 0.565. Twenty minutes after addition of tetrapeptide, solution II was formed with absorption maximum at 520 mμ and ϵ_{max} 0.875, corresponding to the tetrapeptide complex. The process of displacement is represented by scheme 3.



Scheme 3

The tetrapeptide quantitatively cleaves the diglycylglycine complex, as will be shown in the following section. If, however, diglycylglycine is added to the solution of the copper-biuret complex of the tetrapeptide, no changes are observed. The coordination sphere of diglycylglycine is therefore less stable than the coordination sphere of the tetrapeptide, and the cause of its instability is the quaternary coordination bond which, in our opinion, is formed by a water molecule; the development of this bond in the coordination sphere of the complex was evidently the cause of the shift of the absorption maximum of the diglycylglycine complex toward the longer waves by 55 mμ in comparison with the maximum of the tetrapeptide complex.

d) Tetrapeptide was added to the violet solution I of the copper-biuret complex of leucylglycyltryptophan

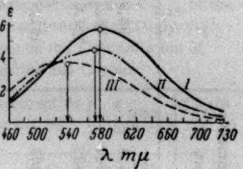


Fig. 5. Spectrophotometric curves. I) Solution of copper-biuret complex of diglycylglycine (0.126%); II) ditto 50 minutes after addition of biuret; III) ditto 100 hours after addition of biuret.

(0.13%). The color changes very quickly and red solution II was formed. The spectrophotometric curves of these solutions are plotted in Fig. 4. Curve I corresponds to the original solution, curve II to the solution formed. The absorption maximum of solution I lies at 580 mμ, ϵ_{max} 0.238; the maximum of solution II at 520 mμ, ϵ_{max} 0.463. Curve II (Fig. 4) corresponds to the copper-biuret complex of the tetrapeptide. In this experiment, again, the incomplete violet complex is quickly and quantitatively decomposed by the tetrapeptide.

e) The question arises whether the exceptional activity of formation of the tetrapeptide complex is simply some individual property of triglycylglycine and not one of the limiting cases in the sequence of stability of biuret complexes. The answer is no, as the following experiment shows. Whereas a biuret complex is easily cleaved by tetrapeptide with formation of a more stable tetrapeptide complex, complexes whose maximum has a longer wave-length than biuret in turn cleave biuret. Thus, for example, if biuret is added to the violet solution I of the diglycylglycine complex (Fig. 5, curve I) the complex is slowly cleaved (Fig. 5). The maximum of the original 0.12% solution of the diglycylglycine complex is at 575 mμ (Fig. 5, I), ϵ_{max} 0.565; 50 minutes after addition of biuret, the maximum is shifted to 570 mμ, ϵ_{max} 0.445 (Fig. 5, II); after 18 hours the maximum has shifted to 560 mμ, ϵ_{max} 0.440; after 100 hours to 535 mμ, ϵ_{max} 0.367 (Fig. 5, III). The character of the absorption of curve III (Fig. 5) corresponds to the biuret complex. Consequently, the diglycylglycine complex is cleaved by biuret, but the process is 300 times slower than with participation of tetrapeptide. It must be pointed out that biuret was added in considerable excess, whereas in the experiments with the tetrapeptide the excess was insignificant.

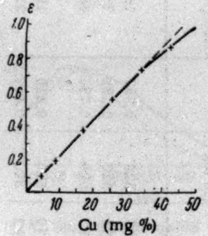


Fig. 6. Optical density (ε) as a function of the copper concentration (in mg %) in solutions of copper-biuret complex of triglycylglycine.

The above-described experiments show that the stability of biuret complexes varies in direct dependence on the composition of the coordination bonds of the complex. Maximum stability is is exhibited by completed red complexes containing four nitrogen-containing groups in the coordination sphere. The latter, however, are not equivalent in this sense; coordination bonds formed by peptide groups that absorb shorter waves are evidently distinguished by greater stability. Due to this, the most stable and the most easily formed is the complex whose coordination sphere contains not less than three peptide groups, as is the case with tetrapeptide complex. A pentapeptide (tetraglycylglycine) must evidently be placed first in order of stability of biuret complexes; the maximum of absorption of this pentapeptide is at 515 mμ. In the light of the foregoing considerations we can conclude that the position of maximum absorption of the copper-biuret complex is a criterion of relative stability. The shorter the waves absorbed by the complex, the greater the stability of the latter. A substance forming a complex with a short-wave absorption maximum will always cleave a complex with an absorption maximum of longer wave-length. The greater difference in the positions of the maxima of absorption of the complexes, the more complete and the more rapid will be the displacement reaction. The resulting complex always has a maximum at a shorter wavelength. The magnitudes of the shift of the maximum, which may be called the "shift increments," show a certain regular trend. Examination of the experimental data led us to the conclusion that

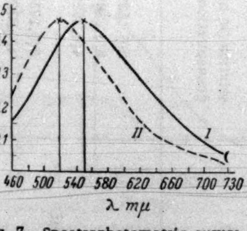


Fig. 7. Spectrophotometric curves. I) Solution of copper-biuret complex of total protein of rabbit muscle (0.175%); II) ditto 20 minutes after addition of triglycylglycine.

TABLE 1

Quantitative Characterization of Reactions of Displacement of Substances from Copper-Biuret Complexes of Triglycylglycine

Substance	Biuret complex of substance			Property of solution after addition of triglycylglycine			Copper number of substance		Degree of displacement (%)
	volume of solution (ml) and its concentration	λ_{max} (in mμ)	ϵ_{max}	λ_{max} (in mμ)	ϵ_{max}	Cu concentration (in mg %)	found by experiment	found iodometrically	
Biuret	4(0.154%)	535	0.256	520	1.1	50.0	195.63	206	105
Leucylglycylasparagine	4(0.105%)	525	0.233	520	0.403	18.5	360.0	386.5	106.9
Diglycylglycine	5(0.126%)	575	0.565	520	0.875	42.5	188.4	186	98.6
Leucylglycyltryptophan	4(0.13%)	580	0.238	520	0.463	21.7	380.8	372.75	98.7

TABLE 2

Quantitative Characterization of Reactions of Displacement of Proteins from Copper-Biuret Complexes of Triglycylglycine

Protein	Biuret complex of protein			Properties of solution after addition of triglycylglycine			Copper number of protein		Degree of displacement (%)
	solution (in ml) and its concentration	λ_{max} (in mμ)	ϵ_{max}	λ_{max} (in mμ)	ϵ_{max}	Cu concentration (in mg %)	experimental value	iodometric value	
Casein	5(0.152%)	550	0.357	520	0.357	16.57	576.5	570	98.9
Gelatin	5(0.238%)	565	0.573	520	0.589	27.5	549.5	547	99.5
Edestin	4(0.268%)	550	0.790	520	0.770	35.5	477.9	486	101.6
Total protein of rabbit muscles	5(0.175%)	555	0.470	520	0.415	19.5	570.5	578	101.3
Insulin	4(0.217%)	535	0.603	520	0.612	29	475.1		

TABLE 3

Dependence of the $\epsilon_{\max}$ of the Biuret Complex of Triglycylglycine on the Concentration of Peptide and Copper

Tetrapeptide (in mg %)	$\epsilon_{\max}$ (λ 520 mμ)	Cu (in mg %)
16.4	0.097	4.23
32.8	0.188	8.46
65.6	0.370	16.92
98.4	0.550	25.38
131.2	0.725	33.84
164.0	0.861	42.3

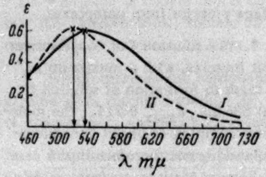


Fig. 8. Spectrophotometric curves. I) Solution of copper-biuret complex of insulin (0.217%); II) the same 20 minutes after addition of triglycylglycine.

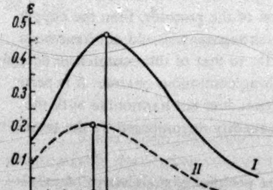


Fig. 9. Spectrophotometric curves. I) Solution of copper-biuret complex of total protein of rabbit muscles (0.175%); II) the same 20 minutes after addition of biuret.

replacement of each complex-forming group in the coordination sphere of a complex by a peptide group leads to the following magnitudes of shift of the maximum toward the shorter wavelengths: replacement of an amino group – 5 mμ, of an amido group – by 5 mμ, of an aliphatic hydroxyl – by 20 mμ, of an ether group – by 45 mμ, of water – by 55 mμ. We do not attach any absolute significance to these values, and we regard them as relative characteristics. It is interesting that replacement of a peptide group in a peptide by any other group [1] leads to shifting of the absorption maximum of a complex in the direction of longer waves; at the same time the shift increments remain the same but are opposite in sign.

2. Quantitative characterization of reactions of displacement of substances from a biuret complex. In this part of the work we investigated the degree of completeness of displacement of one substance by another from copper-biuret complexes with reference to reactions with a tetrapeptide. For this purpose we constructed a concentration graph (Fig. 6) of optical density versus copper content (in mg %) for a solution of the copper-biuret complex of a tetrapeptide. Figure 6 shows that in the range of optical densities up to ϵ 0.7 and copper concentrations up to 30 mg %, solutions of a copper-biuret complex of a tetrapeptide exactly follow Beer's law (these concentrations should therefore be employed for measurements). The degree of completeness of the displacement reaction was found by determination of the concentration of copper in a solution formed after addition of tetrapeptide with the help of Fig. 6. Knowing the concentration of the starting solution of the substance under test, we could calculate the number of grams of this substance corresponding in the complex of 1 g-atom of copper (i.e., the "copper number"). These values were compared with the results of direct iodometric determinations of the copper numbers, and in this way the degree of displacement (in %) was calculated.

Table 1 shows that displacement is nearly 100%; the slight deviations are within the limits of experimental error. Such displacement reactions can evidently serve as a new method of determination of "copper numbers" of substances that form copper-biuret complexes, and also as a method of determination of the concentration of a substance in solution.

3. Displacement of proteins from copper-biuret complexes by low-molecular substances. Previous work [4] led us to the conclusion that copper-biuret complexes of proteins are built up from a large number of low-molecular fragments which are mainly of the type of incompleted violet complexes. In the light of the experiments described above, we should therefore expect proteins to be easily and quantitatively displaced from complexes by substances forming completed red complexes (such as a tetrapeptide). The following experiments confirmed our supposition. a) Addition of tetrapeptide to an 0.175% solution of the copper-biuret complex of the total protein of rabbit muscles causes quantitative displacement of the protein. The maximum of the original solution I of the protein complex was at 555 mμ, $\epsilon_{\max}$ 0.470 (Fig. 7, I); 20 minutes after addition of the tetrapeptide solution II was formed with maximum at 520 mμ and $\epsilon_{\max}$ 0.415 (Fig. 7, II). The copper number of the protein calculated from these data agrees with the iodometric value (Table 2).

b) Addition of tetrapeptide to an 0.217% solution (I) of the copper-biuret complex of insulin (Fig. 8, I) (maximum at 535 mμ, ϵ_{max} 0.603) causes a shift of the maximum to 520 mμ, ϵ_{max} 0.612 (Fig. 8, II). The copper number calculated from these data is 475.1 (Table 2).

c) The tetrapeptide quantitatively displaces gelatin from the copper-biuret complex. The maximum of the starting (0.238%) solution I (Table 2) is at 565 mμ, ϵ_{max} 0.573. Addition of tetrapeptide gives solution II with maximum at 520 mμ, ϵ_{max} 0.589 (Table 2). The copper number calculated from the displacement agrees with the iodometric result (Table 2).

d) The tetrapeptide quantitatively displaces edestin from the copper-biuret complex. The maximum of the original (0.268%) solution I (Table 2) is at 550 mμ, ϵ_{max} 0.790. After addition of the tetrapeptide the maximum is shifted to 520 mμ, ϵ_{max} 0.770 (Table 2). The copper number of edestin determined from this experiment agrees with the iodometric value (Table 2).

e) The tetrapeptide quantitatively displaces casein from a complex. The maximum of the starting (0.152%) solution I (Table 2) is at 550 mμ, ϵ_{max} 0.357. After addition of triglycylglycine the maximum is shifted to 520 mμ, ϵ_{max} 0.357. The calculated copper number agrees with that obtained by the iodometric method (Table 2).

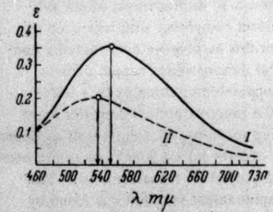


Fig. 10. Spectrophotometric curves. I) Solution of copper-biuret complex of casein (0.152%); II) the same 20 minutes after addition of biuret.

In several experiments it was established that not only a tetrapeptide but also biuret can displace proteins from complexes.

f) Addition of biuret to a 0.175% solution I of copper-biuret complex of total protein of rabbit muscles, with a maximum at 555 mμ, ϵ_{max} 0.470 (Fig. 9, I) leads to formation of solution II (Fig. 9, II) whose maximum is at 535 mμ, ϵ_{max} 0.211. The molecular intensity of the copper-biuret complex of biuret is considerably lower than that of the tetrapeptide, and therefore in this case, as was to be expected, the displacement leads to a considerable lowering of the intensity of absorption.

g) Biuret displaces casein from the copper-biuret complex as shown by Fig. 10. The absorption maximum of the starting (0.152%) solution of the copper-biuret complex of casein lies at 550 mμ, ϵ_{max} 0.353 (Fig. 10, I). After addition of biuret the maximum is shifted to 535 mμ, ϵ_{max} 0.201 (Fig. 10, II). Also in this case the intensity is lowered.

Consequently, biuret complexes of proteins are indeed easily cleaved by tetrapeptide and biuret, i.e., they also behave like incomplete complexes built up from short tripeptide segments. It is perfectly obvious that if longer, continuous peptide chains had taken part in complex formation of the proteins, then the copper atoms would have formed stable segments of the completed complex, and such segments would not have been cleaved by tetrapeptide since each segment would have had a structure similar to that of the complex in accordance with the law that we established for complex formation in the case of long continuous chains. It is particularly noteworthy that the behavior of insulin during the displacement reaction does not harmonize with the ideas about its structure advanced by Sanger [5] since the insulin complex is readily decomposed by the tetrapeptide.

The experiments described in this paper confirm our hypothesis that the position of the absorption maximum of the copper-biuret complex can serve as a criterion of its relative stability: a complex is the more stable the shorter is the wavelength of its absorption maximum.

EXPERIMENTAL

Displacement of biuret from the triglycylglycine complex. 15.4 mg biuret was dissolved in 2 ml 2 N sodium hydroxide, 1 ml 0.25 M copper sulfate was added and the volume made up to 10 ml with water. After an hour, the resulting solution I of the copper-biuret complex of biuret was filtered and spectrophotogrammed in a Beckmann apparatus (Fig. 1). To 4 ml of solution I was added 10 mg triglycylglycine, and after 20 minutes the solution II was examined in the spectrophotometer (the concentration of the solution was halved for the purpose of measurement).

The degree of displacement (%) was calculated as follows. Four ml of starting (0.154%) solution I of copper-biuret complex of biuret contained 6.16 mg biuret. After displacement, the ϵ_{max} (λ 520 m) of solution II was 1.1, which on the copper concentration graph (Fig. 6) corresponds to 50 mg % or 2 mg copper in 4 ml solution II. Before displacement this quantity of copper was bound with 6.16 mg biuret or 1 g-atom per 195.58 g biuret. According to the iodometric determination 1 g-atom copper in the biuret complex corresponds to 206 g biuret. The difference is 5%, i.e., the displacement experiment gave a slightly high result for copper, which must be attributed to experimental errors. The experiment therefore gives a percentage displacement of 105 (Table 2). Similar calculations were made in other experiments. When the copper number in the displacement experiment was determined with an excess, the degree of displacement was less than 100% (Tables 2 and 4).

The plot (Fig. 6) of ϵ_{max} versus copper concentration in solution of biuret complex of triglycylglycine was constructed from spectrophotometric data for six solutions of triglycylglycine complex of definite concentration. Results are presented in Table 3.

Displacement of leucylglycylasparagine, diglycylglycine and leucylglycyltryptophan from biuret complexes of triglycylglycine was effected in a similar manner to that described above. Results are in Table 1 and Figs. 1-4.

Displacement of diglycylglycine from the biuret complex was effected in the following manner. To 4 ml 0.126% solution of copper-biuret complex of diglycylglycine was added 20 mg biuret; since little change occurred in the visible color, another 55 ml biuret was added. The solution was examined with the spectrophotometer after 50 minutes, 18 hours and 100 hours (Fig. 5, II and III).

We synthesized the compounds used in this work by the following methods: triglycylglycine and diglycylglycine by E. Fischer's method [6], biuret by the method of Hofmann [7], leucylglycyltryptophan by the method of Abderhalden, and leucylglycylasparagine by our own method [1].

Displacement of total protein of rabbit muscles from its biuret complex by triglycylglycine was effected under the following conditions: 17.5 mg total protein (total N 14.28%) was dissolved in 2 ml 2 N sodium hydroxide,, 1 ml 0.25 M copper sulfate and 7 ml water. After 2 hours, solution I was filtered and spectrophotogrammed Fig. 7, I). To 5 ml of solution I was added 10 mg triglycylglycine; 20 minutes later, solution II was spectrophotogrammed (Fig. 7, II). The degree of displacement of calculated is described above. For results see Table 2.

Experiments with casein (prepared by Hammarstein's method, total N 14.47%) were run under similar conditions, using a 15.2 mg sample. In experiments with gelatin (total N 14.75%) the sample weighed 23.8 mg; the insulin was a crystalline product, series B-31 of the Factory of Endocrine Preparations (total N 14%), weight 26.8 mg.

Similar conditions were employed for displacement of casein and the total protein of rabbit muscles from the biuret complexes.

SUMMARY

1. It was shown that copper-biuret complexes, which enter into double decomposition reactions, can quantitatively decompose substances that form a biuret complex with an absorption maximum at a shorter wavelength of the visible spectrum.

2. The position of the absorption maximum can serve as a criterion of the relative stability of copper-biuret complexes in these reactions: a complex is the more stable the shorter is the wavelength of the absorption maximum. The greater the difference in the wavelengths of the absorption maxima of complexes, the more rapidly and completely will the displacement of one substance by another proceed.

3. The stability of copper-biuret complexes in double decomposition reactions is a direct function of the composition of the coordination bonds. The most stable is a complex whose inner coordination sphere contains four nitrogen-containing groups although the groups are not equivalent in this sense. A peptide group imparts the maximum stability to coordination bonds. When such a group is replaced in the coordination sphere of a complex by other groups, the maximum is shifted toward longer wavelengths by a definite amount which is characteristic of each group (the "shift increment").

4. A tetrapeptide (glycinic) quantitatively displaces tripeptides (irrespective of their aminoacid composition) from biuret complexes.

5. A tetrapeptide (glycinic) quantitatively displaces proteins (including insulin) from complexes. The displacement reaction can serve as a method of determination of copper numbers.

6. It is shown that the copper-biuret complex of insulin has maximum absorption at a wavelength of 535 mμ; the copper number of insulin is 475.1.

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STUDY OF THE STRUCTURE OF SOME FRUCTOSANS OF PLANTS OF THE FAMILY LILIACEAE

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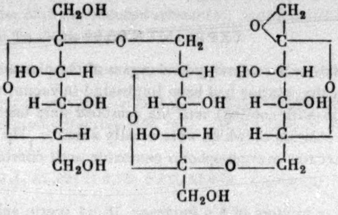
In the present paper we submit the results of a study of the structure of the fructosans that we isolated [1] from the below-ground organs of some plants of the family Liliaceae (Central Asian).

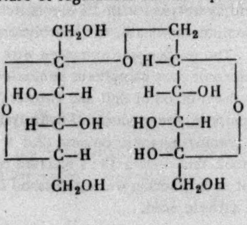
Polygontine is a fructosan of the rhizomes of Polygonatum sewertzowi Rgl. and is a yellow powder with m. p. 207-208° $[\alpha]_D^{20} -52.9°$, which does not reduce Fehling solution. Its half-period of hydrolysis by 1 N H_2SO_4 at 20° is 160 minutes. Empirical formula: $C_{18}H_{30}O_{15}$. Polygontine acetate (m. p. 84-85°) has $[\alpha]_D^{20} -38.86°$ (in chloroform); molecular weight (in benzene) 870; this corresponds to three fructose residues. CH_3CO content 44.8% or 9 groups. The methyl ether of polygontine has $[\alpha]_D^{20} -34.8°$ (in chloroform) and contains 45.6% methoxyl groups. Acid hydrolysis of the methyl ether of polygontine gives 1,3,4,6-tetramethyl-, 1,3,4-trimethyl- and 3,4-dimethyl- fructose in the ratio of 1:1:1. We may suggest formula (I) for polygontine.



(I)

The above formula accounts for the formation of 1,3,4,6-tetramethyl-, 1,3,4-trimethyl- and 3,4-dimethylfructoses in 1:1:1 ratio and for the absence of reducing properties.

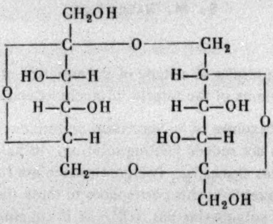
Sogdianose — a difructosan from the roots of Eremurus sogdianus (Rgl.) Benth. and Hook — is a light yellow substance with m. p. 156-158°; $[\alpha]_D^{20} -16.4°$; it reduces Fehling solution; the half-period of hydrolysis by 1 N H_2SO_4 at 20° is 132 minutes; it is hydrolyzed by invertase and ferments with yeast. Empirical formula $C_{12}H_{22}O_{11}$. Sogdianose acetate, with m. p. 94-95°, has $[\alpha]_D^{20} -28.7°$ (in chloroform); molecular weight (in benzene) 670, corresponding to two fructose residues; 8 acetyl groups. The methyl ether of sogdianose with $[\alpha]_D^{20} -40.3°$ (in chloroform) contains 55.1% methoxyl groups. Acid hydrolysis gives 1,2,3,4-tetramethyl- and 1,3,4,6-tetramethylfructoses in 1:1 ratio. The structure of sogdianose can be represented by the formula (II).



(II)

The fructose residues in sogdianose are linked by the 2- and 6-carbon atoms; a pseudocarbonyl group persists at one of the fructose residues and accounts for the reducing properties of the fructosan.

Alliuminoside – a difructosan from the bulbs of Allium sewertzowi Rgl. – is a yellowish substance with m. p. 92-93°, $[\alpha]_D^{20}$ $-23.8°$, half-period of hydrolysis with 1 N H_2SO_4 at 20° 172 minutes; does not reduce Fehling solution; is not hydrolyzed by invertase. Empirical formula $C_{12}H_{20}O_{10}$. The acetate of the difructosan, with m. p. 98-99°, has $[\alpha]_D^{20}$ $-29.3°$ (in chloroform); molecular weight (in benzene) 598, CH_3CO content 44.1% or 6 groups. The methyl ether of the fructosan, with $[\alpha]_D^{20}$ $-39.7°$ (in chloroform), contains 45.3% OCH_3 groups. Acid hydrolysis of the methyl ether gives only 1,3,4-trimethylfructose. The structure of alliuminoside can be represented by formula (III).



(III)

The fructose residues in the difructosan are linked through the 2,6'- and 2',6-carbon atoms. The proposed structure accounts for the absence of reducing power in the difructosan and for the relatively difficult hydrolyzability due to the presence of a dioxane ring.

EXPERIMENTAL

The fructosans were isolated from the below-ground organs of the plants by extraction with water in presence of calcium carbonate. After the solution had been inspissated in vacuo, the product was isolated and purified by reprecipitation with alcohol (with cooling) until the constants were unchanged; it was then tested for the presence of proteins and inorganic substances (which were usually absent). The purified preparations of the fructosans were kept in a vacuum-desiccator over phosphorus pentoxide until constant in weight. They were then investigated.

Preparation of the acetates. A mixture of 3 g fructosan, 15 ml acetic anhydride and 30 ml dry pyridine was allowed to stand at room temperature for 10 hours with frequent stirring. After acetylation, the mixture was run into cold water, and the resulting crystalline mass was carefully triturated with cold water. After suction-filtration, washing with water, and drying in a desiccator over sulfuric acid, the acetate of the fructosan was purified by numerous reprecipitations with ligroine from benzene solution. The specific rotation of the acetate was measured in chloroform, and the molecular weight cryoscopically in benzene.

Preparation of methyl ethers. Haworth's method [2] was used – methylation in acetone solution with dimethyl sulfate and then with methyl iodide in presence of silver oxide. The methyl ethers were purified by reprecipitation with ligroine from chloroform solutions. The specific rotation was determined in chloroforom solution and the molecular weight cryoscopically in benzene. Methoxyl groups were determined by cleavage by Zeisel's method, and the quantity of methyl iodide formed was determined by the Kirpal-Biun method.

Methyl ethers of the fructosans were hydrolyzed with 1% alcoholic solution of oxalic acid on a water bath. for 12 hours. After neutralization with sodium carbonate, the hydrolyzate was decolorized by activated animal charcoal and evaporated down in vacuo. The residue was extracted with ether, the ether was driven off, and the products of hydrolysis were kept in a desiccator over phosphorus pentoxide. The components of the hydrolyzate were fractionated by chromatography by the method of Bell and Palmer [3] as modified by Schlubach and Heesch [4], using a silica gel column. For this purpose, the products of hydrolysis of the methyl ethers (about 1.5 g) were dissolved in 5 ml toluene and put into a chromatographic column (2.5 × 80 cm). The column was developed at first with toluene containing 0.33% ethanol, then with a 19:1 mixture of chloroform and n-butanol, and finally with methanol. Completion of elution of each fraction was established in a separate test with a 1% alcoholic solution of α-naphthol and concentrated sulfuric acid.

Polygontine. Found %: C 44.10, 44.22; H 6.32, 6.28. M 493. $C_{18}H_{30}O_{15}$. Calculated %: C 44.44; H 6.18. M 486.

Polygontine acetate. Found %: C 50.16, 50.05; H 5.68, 5.60; CH_3CO. 45.53, 45.30. M 870. $C_{36}H_{48}O_{24}$. Calculated %: C 50.0; H 5.5; CH_3CO 44.8 (9 CH_3CO- groups).

Methyl ether. Found %: C 53.02, 52.80; H 8.0, 7.98; OCH_3 45.32, 45.50. M 620. $C_{27}H_{48}O_{15}$. Calculated %: C 52.94; H 7.84; OCH_3 45.60. M 612.

Chromatographic resolution of 1.3320 g of products of hydrolysis of the methyl ether of the polyfructosan gave three fractions: 1st, 455 mg (34.16%); 2nd, 422 mg (31.68 %); 3rd 406 mg (30.48%).

1st fraction: n_D^{20} 1.4534, R_G 0.99, $[\alpha]_D^{20}$ +29.58°.

Reduction. 154.6 mg substance: 89.5 mg reduced substance. Found %: 57.87. Found %: OCH_3 52.74, 52.40. $C_6H_8O_2(OCH_3)_4$. Calculated %: OCH_3 52.50.

The substance in the 1st fraction is 1,3,4,6-tetramethylfructose. Literature data [5-8]: n^{20}D 1.4513, R_G 1.01, $[\alpha]_D^{20}$ +30.3°; reduction 55.6%; OCH_3 52.50%.

2nd fraction: n^{20}D 1.4654, R_G 0.83 $[\alpha]_D^{20}$ −48.45°.

Reduction. 146 mg substance: 73.2 mg reduced substance. Found %: 50.12. Found %: OCH_3 41.58, 41.84. $C_6H_9O_3(OCH_3)_3$. Calculated %: OCH_3 41.90.

The 2nd fraction contains 1,3,4-trimethylfructose, since the constants are in agreement with the literature data for this compound [5-8].

3rd fraction: n^{20}D 1.4850, R_G 0.60 $[\alpha]_D^{20}$ −59.38°.

Reduction. 160 mg substance: 83.8 mg reduced substance. Found %: 52.4. Found %: OCH_3 29.52, 30.05. $C_6H_{10}O_4(OCH_3)_2$. Calculated %: OCH_3 29.80.

These constants are in agreement with those reported in the literature for 3,4-dimethylfructose [5-8].

Hydrolysis of the methyl ether of polygontine thus gave 1,3,4,6-tetramethylfructose (455 mg), 1,3,4-trimethylfructose (422 mg) and 3,4-dimethylfructose (406 mg). On the basis of fructose the calculated ratio is 1.014 : 1.0 : 1.02 or very near to 1 : 1 : 1.

Sogdianose. Found %: C 42.4, 42.02; H 6.58, 6.60. M 338. $C_{12}H_{22}O_{11}$. Calculated %: C 42.10; H 6.44. M 342.

Sogdianose acetate: Found %: C 49.40, 49.62; H 5.80, 5.55; CH_3CO 50.40, 50.20. M 670. $C_{28}H_{38}O_{19}$. Calculated %: C 49.55; H 5.61; CH_3CO 50.73 (8 groups). M 678.

Methyl ether. Found %: C 53.0, 52.72; H 8.52, 8.24; OCH_3 55.10, 54.36. M 640. $C_{20}H_{38}O_{11}$. Calculated %: C 52.86; H 8.37; OCH_3 54.62. M 454.

Hydrolysis of the methyl ether of sogdianose was at first carried out with 1% alcoholic solution of oxalic acid, and subsequently with 0.25% solution of hydrochloric acid on a water bath at 80° for 2 hours. Chromatographic resolution of 1.4982 g of products of hydrolysis in a silica gel column gave two fractions: 1st, 736 mg (49.12%); 2nd, 718 mg (48.0%).

1st fraction: n^{20}D 1.4568, R_G 0.99, $[\alpha]_D^{20}$ +31.2°.

Reduction. 152 mg substance: 83.8 mg of reduced substance. Found %: 55.2. Found %: OCH_3 52.90, 52.30. $C_6H_8O_2(OCH_3)_4$. Calculated %: OCH_3 52.50.

The constants found for the 1st fraction agree with those in the literature for 1,3,4,6-tetramethylfructose [5-8].

2nd fraction: n^{20}D 1.4683, R_G 0.85, $[\alpha]_D^{20}$ −48.2°.

Reduction. 145 mg substance: 72.4 mg reduced substance. Found 50.0%. Found %: OCH_3 42.40, 42.05. $C_6H_9O_3(OCH_3)_3$. Calculated %: OCH_3 41.90.

Consequently, the 2nd fraction is 1,3,4-trimethylfructose, which is formed from 1,2,3,4-tetramethylfructose on hydrolysis with 0.25% hydrochloric acid. The methyl ether of sogdianose therefore contains 1,2,3,4-tetramethyl- and 1,3,4,6-tetramethylfructose in the ratio of 736 : 718 mg. On a fructose basis this is equivalent to 1 : 1.03 or close to 1 : 1.

Alliuminoside. Found %: C 44.58, 44.20; H 6.30, 6.25. M 330. $C_{12}H_{20}O_{10}$. Calculated %: C 44.44; H 6.18. M 324.

Acetate. Found %: C 50.12, 49.88; H 5.60, 5.48; CH_3CO 44.6, 45.0. M 584. $C_{24}H_{32}O_{16}$. Calculated %: C 50.0; H 5.56; CH_3CO 44.8 (6 CH_3CO-groups). M 576.

Methyl ether. Found %: C 53.08, 52.80; H 8.0, 7.68; OCH_3 45.35, 45.60. M 415. $C_{18}H_{32}O_{10}$. Calculated %: C 52.94; H 7.84; OCH_3 45.58. M 408.

Analysis by paper chromatography showed that the hydrolyzate of the methyl ether contains only trimethylfructose alone. Before analysis the trimethylfructose was purified by filtration of the toluene solution through a silica gel chromatographic column and washed in the column with a 19 : 1 mixture of chloroform and n-butanol. The resulting trimethylfructose had $n^{20}D$ 1.4650, R_G 0.84, $[\alpha]^{20}_D$ −48.0°.

Reduction. 146.2 mg substance: 73.2 mg reduced substance. Found %: 50.05. Found %: OCH_3 42.2, 41.7. $C_6H_9O_3(OCH_3)_3$. Calculated %: OCH_3 41.90.

The constants of the substance are identical with the literature data for 1,3,4-trimethylfructose [5-8].

SUMMARY

Three fructosans were isolated from the below-ground organs of plants of the Liliaceae. They are genetically related: sogdianose is an intermediate product of hydrolysis of polygontine, and alliuminoside is the anhydride of sogdianose.

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DISCUSSION FORUM

THE PROBLEM OF CONJUGATION IN BENZENE

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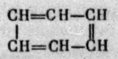
1. Ninety years have passed * since A. M. Butlerov put forward a benzene formula with alternating single and double bonds in a ring [1]. Many dozens of benzene formulas have been proposed since then. However, the formula first proposed



$$\begin{array}{ccccc} CH & = & CH & - & CH \\ | & & & & \| \\ CH & = & CH & - & CH \end{array}$$

by A. M. Butlerov on the basis of Kekulé's ideas on the structure of the aromatic nucleus has again and again been found, on the basis of accumulated chemical and physical data, to be the most suitable representation (see, for example, [8-10]).

At the end of the twenties and the start of the thirties the resonance–mesomeric theory of the chemical bond was originated and developed and gained very widespread acceptance. In applying this theory to benzene Ingold [11] indicated that in the light of the chemical facts relating to benzene the Kekulé formula (i.e., the Butlerov-Kekulé formula – author) is undoubtedly the best. But the theory in question was developed on the basis of the concept of the chemical bond of the Copenhagen school of quantum mechanics (Heitler–London–Pauling–Slater–Ingold). However, from the main premises of this theory were deductively and arbitrarily [11-13] derived (predicted) fundamental physical properties of benzene which conflicted with the Butlerov-Kekulé benzene formula. In considering these properties, Ingold [11] made the following observations: a) the π-electrons of the benzene ring can be delocalized due to hypothetical superposition in benzene of five structures; this superposition requires equalization of the electronic density in the benzene ring throughout all of its CC bonds and therefore implies the equivalence of the latter; b) from this follows directly the symmetry of benzene as a regular plane hexagon – D_{6h} (benzene must have an axis of symmetry of the sixth order, a center of symmetry, CC bonds of equal lengths, etc.); c) this symmetry of the benzene molecule explains the zero dipole moment, the magnetic symmetry in the plane of the ring, etc. etc.

In support of their theory the above authors cited the results of physical investigations. However, when this theory was created in the early thirties, the physical techniques that could assist the understanding of the specific singificance of the individual bonds of the molecule were still rather inadequate, and the enthusiasm for the newly enunciated ideas of the Copenhagen school of quantum mechanics hindered appreciation of a series

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[*] In his papers in 1865 and 1866 [2-4] Kekulé did not extend his ideas about the structure of the aromatic nucleus to benzene itself. At that time he considered acceptable his proposed benzene formula in the form of a hexagon whose sides form single C–C bonds. Only after the appearance in 1868 of a German edition of A. M. Butlerov's course of lectures [1] which gave the above formula of benzene, and only after the formula, had been given in 1869 in a paper by Ladenburg [5] (Ladenburg himself, however, did not accept this formula but proposed other benzene formulas) did Kekulé for the first time in 1869 [6] formulate a benzene ring with alternating single and double bonds, while pointing out that he would shortly attempt to overcome the difficulties that were attached to this formula. This attempt was undertaken in 1872 [7] when he advanced the hypothesis of the oscillating benzene model. It is clear from the foregoing that the structural formula of benzene with alternating double and single bonds, usually associated with the name of Kekulé, should more correctly be called the Butlerov-Kekulé formula.

of very important experiments whose results conclusively refuted the fashionable concept of the structure of the benzene. The current trend in physical thought also led to unrealistic interpretations of the most important direct experiments. We can show that examination of the totality of now available important chemical and physical data does not confirm the foregoing hypotheses on the structure of benzene but rather confirms the Butlerov-Kekulé structural formula.

2. In the thirties the uniformity of the lengths of the CC bonds of benzene was demonstrated by ignoring the serious experimental errors that were then inherent in electron diffraction and x-ray investigations. Determinations by different authors led to the following results (among others) for the length of the CC bond of benzene: 1.39 ± 0.03 A [14], 1.39 ± 0.02 A [15], 1.42 ± 0.03 A [16]. These data give ample reason for asserting that the CC bond lengths in benzene are undoubtedly smaller than the length of the single C−C bond (approx. 1.54 A in ethane) and slightly larger than the double C═C bond (approx. 1.33 A in ethylene). They do not, however, confirm the conventional equivalence of all of the CC bonds in benzene since in the above-cited investigations the neglected difference in lengths of the bonds in question is respectively in the range of 1.36-1.42 A, 1.37-1.41 A, 1.39-1.45 A, etc. These are very significant limits of experimental error and could conceal a possible geometrical asymmetry of the benzene ring. Later, more accurate, electron diffraction investigations of benzene in the gas phase [17] established that the benzene molecule is plane but not necessarily characterized by D_{6h} symmetry with two equal ortho- and meta- distances. Later electron diffraction data likewise afford good evidence for a model with splitting of each of these distances into two:

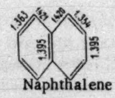
$$\text{ortho}\begin{cases}1.393 + a \pm 0.005\\ 1.393 - a \pm 0.005\end{cases};\quad \text{meta}\begin{cases}2.41 + b \pm 0.015\\ 2.41 - b \pm 0.015\end{cases};\quad \text{para } 2.786 \pm 0.015;\ \text{CCC angle}\begin{cases}120^\circ + 80\\ 120^\circ - 80\end{cases}$$

where $0 \leq a < 0.03$; $0 \leq b < 0.05$.

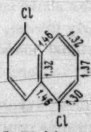
According to these data the (1, 2) and (1, 6) ortho distances can be respectively 1.396 and 1.390 A, the (1, 3) and (1, 5) meta positions can be 2.46 and 2.36 A, which are outside the limits of experimental error. But if these CC ortho- and meta- distances are split into two, then the axis of symmetry of the molecule is of the third and not of the sixth order [17], i.e., the molecule has D_{3h} symmetry (the molecule is plane, a center of symmetry is absent, etc.).

X-ray examination of crystalline benzene at −3° was carried out in 1954 [18] and confirmed the plane structure of the benzene ring, but at the same time revealed a slight difference between the CC bond lengths (± 0.0033 A within the limits of experimental error) and bond angles, i.e., a slight asymmetry of the benzene ring: $C_1C_2 = 1.377$ A, $C_2C_3 = 1.382$ A, $C_3C_4 = 1.374$ A; $\angle C_6C_1C_2 = 119^\circ 28'$, $\angle C_1C_2C_3 = 120^\circ 49'$, $\angle C_2C_3C_4 = 119^\circ 42'$. According to these data the single bond in benzene is approx. 1.382 A and the double bond approx. 1.375 A. These differences are outside the range of experimental error.

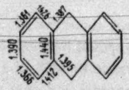
We may note that at the present time the nonequivalence of the CC bond lengths has been conclusively established [19] for a very large number of polynuclear aromatic systems, both condensed and uncondensed, as well as for some substituted benzenes. We present the following examples (distances in A):



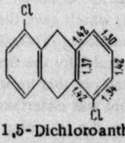
Naphthalene



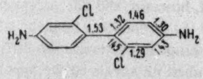
1,5-Dichloronaphthalene



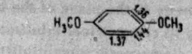
Anthracene



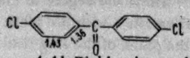
1,5-Dichloroanthracene



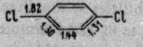
2,2'-Dichlorobenzidine



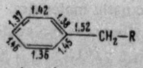
p-Dimethoxybenzene



4,4'-Dichlorobenzophenone



p-Dichlorobenzene



Potassium benzylpenicillide•

The nuclear skeleton of the benzene ring is thus markedly compressed at the single bonds; the length of the latter is closer to that of the ethylene double bond than to the ethane single bond. The ring is slightly asymmetrical; the symmetry of the benzene nucleus is lower than D_{6h}.

3. On the assumption of D_{6h} symmetry of benzene in the theory considered above, it is concluded that the dipole moment of benzene and its symmetrically substituted derivatives is zero [11, 13, 20]. But even Smythe [21] could not say conclusively that such compounds had zero moment; it was also reported that the moment of benzene would in any case be very small; in agreement with a series of experimental determinations he found a value of $0.2 \cdot 10^{-18}$ for the dielectric constant of benzene. According to recent determinations benzene has a dipole moment ($\mu \cdot 10^{18}$) in hexane solution of 0.08, in carbon tetrachloride of 0.06, in carbon disulfide of 0.09 [22]. In an extensive study of the dipole moment of 47 derivatives of benzene, Tiganik [23] found small values for para-di- and symmetrically disubstituted derivatives of benzene, but they were quite different from zero (in the range 0.12-0.70), whereas the value would have been zero in the event of equivalence of the bonds of benzene and the benzene nucleus. The reality of the small dipole moments found is also demonstrated by the constancy of a series of ratios. Thus, according to the concept under consideration the following values would result for the ratios of the moments of di- and symmetrically tri-substituted benzenes with the same substituents to the moments of the corresponding monosubstituted compounds [21, 23].

$$\frac{\mu_{\text{ortho}}}{\mu_{\text{mono}}} = 1.73; \quad \frac{\mu_{\text{meta}}}{\mu_{\text{mono}}} = 1; \quad \frac{\mu_{\text{para}}}{\mu_{\text{mono}}} = 0; \quad \frac{\mu_{\text{sym. tri}}}{\mu_{\text{mono}}} = 0.$$

Actually, however, these ratios are substantially constant for the investigated derivatives; they are different from the values demanded by the above theory, and (most important of all) the last two ratios are not equal to zero; they are respectively approx. 1.420, 0.945, 0.144 and 0.178. The reality of the observed small moments of symmetrically substituted benzenes is also evidenced by the substantial identity between the moments of the trisubstituted mesitylenes and of the sum of the moments of the corresponding trisubstituted benzenes ($\mu \cdot 10^{18}$):

Trichlorobenzene	0.28	Tribromobenzene	0.28	Trinitrobenzene	0.70
Mesitylene	0.07	Mesitylene	0.07	Mesitylene	0.07
Total	0.35	Total	0.35	Total	0.77
Trichloromesitylene	0.38	Tribromomesitylene	0.35	Trinitromesitylene	0.79

The dipole moments of hexasubstituted benzenes with identical substituents are not zero but range from 0.1 to 0.79 [23].

Consequently the existing experimental data testify to dipole moments that differ from zero in the case of benzene as well as its symmetrical derivatives, thereby proving that benzene does not possess D_{6h} symmetry.

4. According to the concept under consideration, the delocalization of the six π-electrons was considered to be confirmed by the considerable anisotropy of the magnetic susceptibility of benzene in the direction perpendicular to the plane of the ring; this anisotropy is explained by the hypothesis that all of the six π-electrons of the benzene molecule can describe a complete circle round the whole of the benzene ring without any localization of them [11, 24].••

• Only the phenyl and the attached methylene group is written out; the remainder of the molecule is represented by R.

•• In this connection benzene has been likened to a metal in which the π-electrons are an electronic gas. Calculations have been made for benzene on this basis [25].

This movement must affect the degree of magnetic symmetry in the plane of the benzene ring itself. This hypothesis, however, is at variance with the facts: benzene and its symmetrical substituted derivatives possess magnetic asymmetry in the plane of the ring itself. Thus, the diamagnetic susceptibility of hexamethylbenzene is highest along the magnetic axis perpendicular to the plane of the benzene ring ($K_3 = -163.8 \cdot 10^{-6}$); this is also true of all planar aromatic molecules. But the susceptibilities in the directions of the other two magnetic axes of the hexamethylbenzene molecule, perpendicular to K_3 and therefore lying in the plane of the ring, differ from one another: $K_1 = -101.1 \cdot 10^{-6}$; $K_2 = -102.7 \cdot 10^{-6}$; moreover the K_1 direction forms an angle of about 100° with the line passing through the center of one pair of carbon atoms and methyl groups; this straight line forms a right angle with the K_2 direction. Krishnan [26] emphasizes that the anisotropy of the diamagnetic susceptibility in the (001) plane of the benzene ring lies outside the limits of experimental error. In this connection he writes: "We must draw attention to the small but definite anisotropy in the (001) plane," i.e., in the plane of the benzene ring. In the same connection Selwood writes [27] that we can assume that benzene itself does not possess magnetic symmetry in the plane of the ring because the two principal susceptibilities in the plane of the ring are slightly different from one another in the case of any of the investigated derivatives of benzene. This is observed both for mono- and polynuclear (uncondensed and condensed) aromatic molecules. In such symmetrical polynuclear molecules as stilbene ($C_6H_5-CH{=}CH-C_6H_5$) and diphenylacetylene ($C_6H_5-C{\equiv}C-C_6H_5$) "extremely high anisotropy in the plane of the molecule" is found [28] (see Table 1).

TABLE 1

Principal Magnetic Susceptibilities of Some Molecules ($K \cdot 10^6$) [26-29]

Molecule	k_1	k_2	k_3
Hexamethylbenzene	−101.1	−102.7	−163.8
1,2,4,5-Tetramethylbenzene	− 77.3	− 85.6	−140.7
p-Benzoquinone	− 24.2	− 27.9	− 68.0
Stilbene	− 85.8	− 50.1	−209.6
Diphenylacetylene	− 81.5	− 67.8	−198.5
Naphthalene	− 39.4	− 43.0	−187.2
Anthracene	− 45.9	− 52.7	−272.5
β-Naphthol	− 46.6	− 50.2	−194.4

The experimentally established diamagnetic anisotropy in the plane of the benzene ring is not consistent with D_{6h} symmetry of benzene; it is caused by unequal distribution, relative to the K_1 and K_2 axes, of the π-electrons with localization of the latter pairwise in three conjugated double bonds. The anomalously high magnetic anisotropy along the K_3 axis can be associated only with restricted movement of electrons in three conjugated double bonds in the plane of the ring. Considerable support for this hypothesis is afforded by the circumstance that the high diamagnetic anisotropy in the direction perpendicular to the plane of the molecule is characteristic not only of aromatic compounds (where it is particularly marked) but also of other substances with conjugated double bonds – ketones, fatty acids, esters of fatty acids and unsaturated alcohols – in which there can be no question at all of any restricted circumscribing movement of electrons throughout the whole of the molecule [28-29]. In the case, for example, of maleic acid with its three conjugated double bonds, which are not constrained into a valence ring, the diamagnetic anisotropy [30] is more than three times as high as that of benzene, although it would be impossible to apply here the theory of London (on the free movement of π-electrons throughout a benzene ring [28]).

5. As far back as the end of the 19th century, Brühl [8] investigated the change of molecular volumes in the series of cyclohexane–cyclohexene–cyclohexadiene–benzene. He established that the progressive contraction in the above order of the series is substantially identical for each member and is roughly the same as in the corresponding series of aliphatic compounds* (See Table 2).

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* We have corrected the data in accordance with the later data for atomic weights and densities.

TABLE 2

Compound	Molar volume at 20°	Contraction in volume
Cyclohexane	108.13	
Cyclohexene	101.47	−6.66
Cyclohexadiene	95.26	−6.21
Benzene	88.85	−6.41

The volume of benzene is an additive magnitude [10]; it can be calculated from the well-known formula of Kopp, with allowance for the contraction due to the three double bonds.

6. Brühl calculated the theoretical magnitude of the molar fraction of benzene on the assumption that the molecule contained three ethylenic bonds; his value was in agreement with the experimental one. At the present time the absence of an exaltation of refraction in benzene is well authenticated; its molar refraction is an additive magnitude (equal to the sum of the refractions of the six C−H bonds, three C−C bonds and three C=C bonds).

On the basis of his investigations on the molar volume and molar refraction of benzene, Brühl [8] concluded that benzene must contain ethylenic bonds (three). This is consistent with all of the data considered above, supports the Butlerov-Kekulé structural formula of benzene, and refutes the previously considered hypothesis that three conjugated double bonds are absent from benzene. Supporters of the latter theory attribute the additivity of refraction in benzene to its alleged nonpolarity (see [12], p. 244) or even more simply to the fortuitousness (!) of this additivity in benzene (see [31], pp. 282 and 209), thereby ignoring the fact that their theory is at variance with experiment.

7. If the benzene molecule had D_{6h} symmetry it should possess a center of symmetry, and an alternating prohibition should ensue: the Raman spectrum should not contain frequencies of the infrared absorption spectrum, and conversely. In the spectra of liquid benzene, as we found in agreement with other authors [11, 22] the alternative prohibition is not manifested; the Raman spectrum contains the "prohibited" (according to Ingold and others) frequencies of 685, 1033 and 1480. Consequently, the molecule of liquid benzene lacks D_{6h} symmetry. But chemical evaluations of the reactivity of benzene and of its properties are made in the overwhelming majority of cases precisely on the basis of the reactions of liquid benzene.

Ingold's alternative prohibition has indeed only been established for benzene in the vapor phase. Two facts must be remembered, however, when we consider the value of this observation for solution of the benzene problem. The absence of the alternative prohibition in the liquid phase of benzene has been directly demonstrated by experiment (measurement of the corresponding frequencies). Occurrence of the alternative prohibition in the gas phase is inferred from the absence of the corresponding frequencies. But the frequencies involved have low intensity in the respective spectra (Raman and infrared), and they are not always observed even in the spectrum of liquid benzene.* They are still more difficult to detect in the vapor phase, especially in the Raman spectra. The experiment in question cannot be considered decisive for determination of the symmetry of benzene in the vapor phase, especially since the vapor phase is used in the electron diffraction investigations; but they do testify, in harmony with other data, to the probability (with a certain degree of approximation − see above) of D_{3h} rather than D_{6h} symmetry. This assertion is convincingly supported by the following observation by Herzberg [34]: "By the symmetry of a molecule we understand the symmetry of configuration of its nuclei; i.e., its nuclear skeleton. The position and type of the nuclei determine its symmetry." As we have seen, the geometry of the nuclear skeleton of benzene, neglecting the third place, is close to D_{6h} symmetry, and only when the third place is taken into account does it become apparent that the symmetry is lower. This closeness of benzene to D_{6h} symmetry (which it does not possess) also makes the development in the vapor phase of the substance of all the physical properties of the molecule that correspond to the actual symmetry which is lower than D_{6h}; in particular it makes the appearance in the spectra of the above-mentioned weak frequencies so that the impression of the alternating prohibition is created. The mechanical criterion here considered is too rough in the present case to reflect the extremely fine but fundamentally important details of the structure of the benzene molecule.

8. In the Raman spectrum of benzene are observed two frequencies at 1584 and 1605 cm^{-1} in the region characteristic of a double bond; in the infrared spectrum one principal frequency is observed at 1617 cm^{-1},

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* In the second paper of [33], for example, they suggested that failure to detect the frequencies might be due to insufficient exposure, poor sensitivity of the photographic plates, etc.

which is also exhibited by the spectrum of C_6D_6 [11, 34]. The resonance-mesomerism theory, which denies the existence of double bonds in benzene, interprets the above-noted Raman frequencies on the basis (see above) of the experimentally unsupported model of benzene with D_{6h} symmetry, as well as on the basis of Wilson's theory [35] which has now been refuted by a body of experimental material. According to this theory [11, 35] the Raman spectrum of benzene contains not two principal frequencies but one principal frequency at 1595 cm^{-1} which splits into two due to Fermi resonance, and the latter is allegedly caused by the fortuitous coincidence in the benzene spectrum of the principal frequency in question with the natural frequency 606 + 992 = 1598 cm^{-1}. The alleged fortuitous effect is proved, according to Wilson, by the fact that the Raman spectra of benzene derivatives contain only one line in the 1600 cm^{-1} region, and a doublet is not observed in any of them. Thus the doublet of frequencies in the region of the double bond is found to be "eliminated" from the benzene spectrum, and the normal 1595 cm^{-1} frequency is arbitrarily assigned to one of the vibrations previously assumed for benzene by the authors of the above-mentioned D_{6h} benzene model (vibrations of the two halves of the molecule relative to one another). But these speculations are in crass contradiction with the now available body of experimental material which largely did not exist at the time of publication of Wilson's work and which shows that, without exception, all compounds with a benzene nucleus possess a frequency in the double-bond region, and in the overwhelming majority of cases in the form of a doublet.* This is true (again in the overwhelming majority of cases) even when Fermi resonance is completely absent. It is clear also that in benzene the doublet in the double-bond region is not associated with fortuitous conditions for the development of the Fermi resonance but with the same factors that come into play in all other compounds with a benzene ring. At the same time the hypothesis of the presence of one normal frequency at 1595 cm^{-1} in the double-bond region must of course be rejected for several reasons: a) there is no such frequency in the benzene spectrum but there is a doublet; b) this frequency was assigned on the basis of the hypothesis of D_{6h} symmetry of benzene, which is not only not confirmed by the experimental data but is refuted by them; c) none of the hitherto investigated hydrocarbon molecules or their substituted derivatives has been found to possess a principal frequency (we are not concerned here with proper frequencies) except when double bonds have been absent from the molecule; similarly the frequency of the vibrations of two halves of the molecule relative to one another (as arbitrarily assumed by Wilson) cannot be developed in this region due to the magnitude of their masses; frequencies of this type of vibrations are usually observed in a region very much lower than even 1000 cm^{-1}.

The presence in the benzene spectrum of principal frequencies in the double-bond region is an experimental fact which testifies to the presence in the benzene ring of three conjugated double bonds. Their interaction leads to the usual resolution of the characteristic frequency; in the present case three components are formed: 1) the frequency of the unsymmetrical vibration of the double bonds (1617 cm^{-1}) appears in the infrared spectrum; 2) a symmetrical vibration frequency appears in the Raman spectrum; due to the possible interaction with the frequency of the pulsating vibration of the ring (992 cm^{-1}) it splits into two – 1584 and 1605 cm^{-1} (these vibrations are executed respectively in the positions of maximum extension and compression of the ring, in which the molecule exists for the longest time during the period of pulsating vibration).

The antisymmetrical vibration is the cause of the actual symmetry of the nuclear skeleton of benzene (averaged over the whole of the vibrational states) being lower than D_{3h} (see above) in the liquid and vapor phases and in the solid state, at any rate in the temperature region remote from absolute zero.

9. The interaction in benzene of three conjugated double bonds is confirmed not only by the splitting of the double-bond frequency but also by the shift of the ultraviolet absorption band into the longer wave region in comparison, for example, with 3-octene (one double bond), 1,3-butadiene (two double bonds). This absorption band is present in benzene at the same level as in hexatriene (3-octene, 185; 1,3-butadiene, 217; hexatriene, 258; octatetraene, 296; benzene, 255 $m\mu$ [36]). This interaction of three localized conjugated double bonds (their electromagnetic and other fields) leads to contraction of the three single bonds of benzene (as it were under an "external" force) without imparting to them a new quality – double-bond character, since this would have required the possession by them of a second pair of electrons; the latter, however, remain localized in the neighboring (double) bonds. Reserve forces are available for this type of contraction "from outside" in

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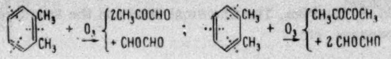
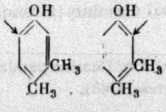
* Thus the Raman spectra of 23 benzene derivatives are described in the second publication cited in [33], and each of these spectra (without exception) contains a doublet in the double-bond region. A frequency doublet in the same region is likewise present in the spectra of 15 organosilicon compounds with a benzene ring that we investigated.

the case of single CC bonds, since the forces of repulsion between their carbon atoms are still far from their maximum; they are close to that in the acetylenic bond in which the length of the CC bond is shortened already to approximately 1.20 A.[*] The consequence of all this is that the nuclear skeleton of benzene becomes markedly and slightly unsymmetrically compressed: whereas in cyclohexane the CC bond length is about 1.53 A, in benzene (see above) the length of the single CC bond is approx. 1.382 A and that of the double CC bond is approx. 1.375 A, i.e., slightly increased.[**] The nuclear skeleton of benzene has a symmetry close to that of D_{6h} model, and only when the third place is taken into account is its true, lower symmetry manifested; the latter, however, can only approximately (see above) be said to correspond to D_{3h} symmetry. The interaction of the three pairs of π-electrons imparts additional stability to the benzene ring; it also leads to some lowering of the electronization of the double bonds in benzene (and in turn to a lowered reactivity), as indicated by the relatively low double-bond region in the spectrum of benzene. In cyclooctatetraene the mechanical and electromagnetic interactions of the four conjugated double bonds are more complex, as is reflected in a larger number of frequencies in the double-bond region which are shifted a relatively long distance toward the higher frequencies (in the Raman spectrum): 1570, 1604, 1635, 1654, 1744 cm^{-1}). This behavior is an indication that cyclooctatetraene passes through a vibrational state in which its double bonds are highly electronized and reactive, so that cyclooctatetraene is lacking in aromatic character.

10. Levine and Cole [37] ozonized o-xylene after proposing that it exists as a mixture of two isomers – 1,2 and 1,6. In the products of ozonization they indeed found all of the substances to be expected on the basis of such a hypothesis (glyoxal, methylglyoxal and diacetyl):



Diepolder and Mills and Nixon [38] coupled diazo compounds with 1,3,4-xylenols and obtained two products, as would be expected if 1,3,4-xylenol exists in two forms (in one of which there are two methyl groups at a double bond and in the second two methyl groups at a single bond) and if coupling always takes place in a carbon chain linked to the hydroxyl group by a double bond:



These and other similar results of chemical experiment [39], in agreement with all of the facts presented above, must be regarded as direct chemical evidence of the existence in benzene and benzene rings of three conjugated double bonds.

SUMMARY

The existing experimental data do not confirm the D_{6h} symmetry of the benzene molecule; they support the Butlerov-Kekulé formula of the structure of benzene with three conjugated, slightly elongated double bonds and three shortened single bonds in a ring. This molecule is only approximately characterized by D_{3h} symmetry and in fact possess a lower symmetry.

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[*] Cases have been observed in which the whole skeleton of a molecule causes the double bond to be stretched to the level of a single bond (see above data for anthracene), so that the double bond containing a pair of π-electrons nevertheless loses the characteristics of a double bond (characteristic length and in turn the characteristic frequency, etc.).

[**] See [40] for more details.

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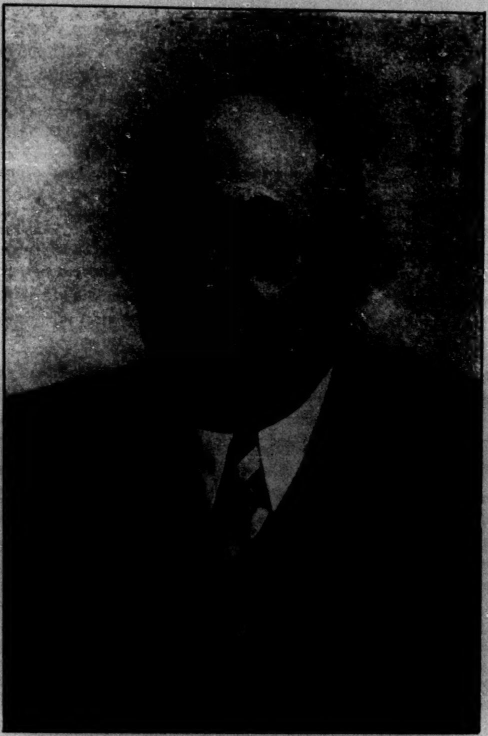


Stepan Nikolaevich Danilov

Highly esteemed and dear Stepan Nikolaevich.

The Editorial Staff of "The Journal of General Chemistry," its authors and its readers congratulate you warmly on your seventieth birthday, forty-fifth anniversary of your scientific teaching activities and fortieth anniversary of your association with the editorial staff of the Journal and wish you good health for many years to come and further fruitful work to the good of our Motherland and Soviet science.

This reaction, first performed by S. N. as a hydroxyketone-saccharinic rearrangement, was confirmed by the reactions of several hydroxyaldehydes [20-22, 30, 38]. It was shown that isomerization of aldehydes of the aliphatic series may occur under the conditions of the dry distillation of wood [24]. It is important to note that the simplest models for epimeric conversions of monosaccharides, that had been known for a long time, were provided by S. N.'s work.

A study of the isomerization of haloaldehydes to acids made it possible for S. N. to explain correctly a number of works by other authors, who had explained them erroneously. On the other hand, the hypotheses S. N. put forward on the mechanism of glycol, aldehyde and hydroxyaldehyde reactions gave an opportunity to other authors to plan and carry out new experimental investigations.

S. N. and N. S. Tikhomirova-Sidorova together devoted some interesting work to the mechanism of hydroxyaldehyde reactions. In this work, the experimental data on the isomerization of hydroxyketones and chloroketones were confirmed for the first time polarographically [79, 93-95].

The very wide investigations S. N. carried out in the field of carbohydrates are closely related to his work on the isomeric reactions of aldehydes and hydroxyaldehydes. In the former field, he also obtained numerous, valuable results [26-28]. In 1936 S. N. and A. M. Gachokidze (50-52) worked out the isomerization of 2-bromoacetomonosaccharides to desonic acids. Later on Gachokidze successfully developed the work in this direction and obtained very interesting new data on isomeric reactions of monosaccharides and disaccharides.

S. N. and his colleagues achieved the epimerization of glucose and fructose by a new method — heating with pyridine, epimeric and degradative conversions of cellulose in the presence of lime, the acetolysis of cellulose, etc.

With I. S. Lishanskii, he investigated the amination and guanidination of monosaccharides, starting with their α-anhydrides [88, 89, 100]. These investigations gave a whole series of new and important facts, which served as a basis for new methods of synthesis in the sugar group. These works were valuable in connection with the chemistry of streptomycin.

Isomeric reactions of carbonyl and hydroxycarbonyl compounds are related to various biochemical processes of carbohydrates and were examined by S. N. in the light of concepts of inter- and intramolecular oxidation-reduction. These concepts can be widely used by physiologists and biochemists. S. N. himself proposed a simple scheme for the formation of lactic acid from glyceraldehyde through β-hydroxyoxide forms, similar to a saccharinic rearrangement.

S. N.'s investigations on the isomeric reactions of carbonyl and hydroxycarbonyl compounds have been generally accepted as classical and have brought him world recognition. One should note that in his works, directed mainly towards the study of isomeric reactions, S. N. also obtained extremely important and valuable material for developing the synthesis of many new substances as well as many unknown organic compounds.

Some of S.N.'s work was devoted to various syntheses in the field of lowmolecular compounds and of this work the following are the most important: the preparation of β-hydroxyketones by hydration of acetylene alcohols [33], syntheses of esters by V. E. Tishchenko's reaction [10], the synthesis of vinylcyclohexylcarbinol [49] and a convenient laboratory and technically suitable method of preparing benzyl ethers of glycerol and ethylene glycol, which are extremely valuable as plasticizers of cellulose esters [31, 41, 45]; together with his colleagues developed a synthesis of enanthol and undecylenic acid by decomposing esters of castor oil and, starting from the latter, prepared azelaic and sebacic acids [109, 110]; they discovered the reasons for poisoning of nickel catalysts by carbon monoxide during the hydrogenation of aliphatic oils [37] and investigated the reactions of amines with chloroamines [83].

S. N. initiated a study of the reaction of α-oxide rings with ammonia, water, hydrogen sulfide, etc [90] in the university laboratory. These reactions were later studied in detail by V. F. Martynov and are very valuable for the synthesis of antibiotics. S. N. also suggested that the reaction of nitrosyl chloride with olefins be investigated thoroughly [91] and this was carried out by K. A. Ogloblin.

S. N. has published monographs and critical reviews on molecular rearrangements [101, 129, 138], on the sequence and role of intermediate compounds in isomeric reactions [139], on sugar chemistry in Russia [136], on simultaneous oxidation-reduction reactions and molecular rearrangements [101, 137], etc. S. N. has also published a large number of papers on the history of chemistry, contemporary problems in organic chemistry [114, 133-135] as well as some devoted to A. M. Butlerov [127-132], A. E. Favorskii [119-126], S. V. Lebedev [118], etc.

The wide and thorough investigations on isomeric reactions of carbonyl and hydroxycarbonyl compounds and the extensive theoretical and experimental material that S. N. had accumulated allowed him to turn to the study of high-molecular compounds such as polysaccharides, cellulose, viscose, etc. This change was not accidental, it was the culmination of a highly logical and successive development of ideas and concepts, worked out by S. N. in numerous investigations on isomeric reactions.

S. N. never tended to work out only the theoretical problems of science. The basis of S. N.'s methodology was, and is, the principle of the interrelation of theory and practise. This is fully confirmed by his wide and active participation in the development of various branches of the chemical industry. During the First and Second World War S. N. was wholly occupied with work connected with war requirements. All this together resulted in S. N.'s interest in high-molecular compounds, which have a tremendous theoretical and practical value.

Among S. N.'s works in the field of polysaccharides and cellulose, we should note those on cellulose, chitin, alginic acid and their derivatives. He investigated the various properties and methods of preparing cellulose ethers and esters, thoroughly studied the properties of nitrocelluloses and obtained new data for the development of the theory on cellulose nitration. In a study of the effect of acids [82, 104] and alkalis [117, 141] on cellulose, the formation of molecular compounds and the effect of swelling on the properties of hydro- and hydrated cellulose were established. In a study of the composition and vapor pressure of nitric acid in phosphoric-nitric acid mixtures, the relation of nitric acid vapor pressure to the presence of certain phosphoric acid hydrates was found [68]. It was shown that in treating cellophane with glycerol the cellulose took out the glycerol trihydrate, described by D. I. Mendeleev, from the aqueous glycerol [75]. It was shown that swelling and solution of cellulose in phosphoric acid was a new method of preparing heat-insulating materials of low specific gravity from cellulose and wood pulp [74]. A new method for characterizing the reducing capacities (copper numbers) of the hydrated cellulose fibers of a viscose filament compressed during extrusion was developed and involved heating the cellulose in Schweitzer's solution [67].

Extensive investigations were carried out on the conditioning of cellulose for the artificial fiber industry [32]. Surveys were published on the characteristics of cellulose [116] and on the determination of molecular weights [140]. It was established that in cuprammonium solutions of cellulose, there are molecular compounds of cellulose with bases, as in alkali cellulose [98, 103]. S. N.'s work provided new data on the synthesis of desoxycellulose, anhydrocellulose and celluloseens, new methods of synthesis were found and the main properties of these almost unknown products characterized [102]. New data on the synthesis and properties of glycerol ethers of cellulose were obtained and the properties of soluble linear and cross-linked molecules of this ether described [66].

Using simple models, in his work S. N. examined the synthesis of plasticizers (benzoyl esters of ethylene glycol and glycerol), the synthesis of benzyl cellulose [41] and developed a more rapid method for determining the composition of benzyl ethers of cellulose by converting the benzyl groups to pentabromotoluene with aluminum and bromine [40]. The conditions for synthesizing carboxymethyl cellulose were studied [35] and this is now produced in large quantities in our factories for use as a lubricating material for boring and as detergents. The colloidal-chemical properties of ethyl and benzyl cellulose were characterized [46, 48]. Unsaturated ethers of cellulose were studied in connection with oxidation polymerization to form three-dimensional structures [78]. S. N. devoted a large number of papers to the study of nitrocellulose. The solution of cellulose nitroesters in various solvents was thoroughly investigated [70, 39]. The role of catalytic phenomena in the synthesis of cellulose esters and the synthesis of high-molecular compounds, in general, was examined critically [141].

A series of S. N.'s investigations were devoted to a study of alginic acid [99] and to the polysaccharide – chitin – which has been studied little [96, 97, 111]. He devoted extensive work to the chemistry and technology of viscose and cuprammonium spinning solutions. These investigations contain original data, which explain substantially the chemistry of viscose and cuprammonium solutions. The results of these works have been incorporated into text books on artifical fibers.

In this review we have noted only very briefly the most important work S. N. has carried out in various fields. A large number of papers describing work that was carried out at S. N.'s suggestion, under his direction and with his advice were published at various times under the names of his co-workers. Even from this brief review one can see how varied and productive S. N. Danilov's activities have been in the scientific, teaching, administrative-organization and social fields.

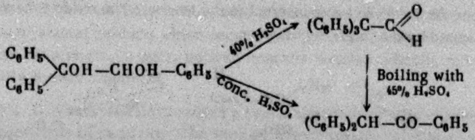
THE WORKS OF S. N. DANILOV IN THE FIELD OF ISOMERIC CONVERSIONS AND MOLECULAR REARRANGEMENTS OF CARBONYL AND HYDROXYCARBONYL COMPOUNDS AND CARBOHYDRATES AND THEIR THEORETICAL IMPORTANCE

T. I. Temnikova, A. N. Anikeeva and N. S. Tikhomirova-Sidorova

During the 45 years since S. N. Danilov's first works on the problem of molecular rearrangements and isomeric conversions of oxygen-containing organic compounds, the concepts in this field of theoretical organic chemistry have evolved considerably. At present, one may consider it established that molecular rearrangements, complicating the course of basic chemical processes in organic chemistry (substitution, cleavage and addition), result from the kinetic tendency of the process to proceed with the migration of hydrogen atoms or hydrocarbon groups to adjacent positions; as regards equilibrium isomeric conversions, which in certain cases proceed very rapidly under the effect of catalysts specific for these conversions, they depend on the thermodynamic factor, as do all equilibrium processes.

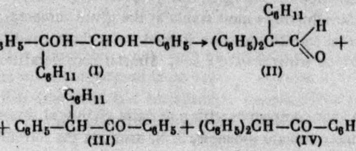
When in 1913, at the suggestion of his teacher, A. E. Favorskii, S. N. began the study of molecular rearrangements, observed during the treatment of α-glycols with mineral acids, many of the details of the concepts mentioned above were very unclear and the works of S. N. were very important in the development of contemporary ideas in these fields of theoretical organic chemistry. In spite of a series of quite convincing experimental data, at that time many investigators still believed in the formation of intermediates (oxides, full ethers of α-glycols and vinyl alcohols) in the rearrangement processes. The most outstanding foreign chemists, working in the field of molecular rearrangements (Tiffen and Meerwein), in examining the reasons why the reaction proceeded mainly or wholely in one of several theoretically possible directions, considered only the structure of the original glycol, the difference in stability of the bonds of the two hydroxyls and the different migration capacity of hydrocarbon groups; the latter was even considered a characteristic property of the group.

As a result of thorough, lucid work and brilliant experimental skill, S. N. Danilov, one of Favorskii's most talented students and faithful followers of the fundamental dialectic conceptions of Butlerov and Favorskii, not only solved a series of individual, confusing problems, but approached the investigation of this field in an essentially new way. Even in his first article devoted to the dehydration of secondary-tertiary α-glycols of hydrobenzoin derivatives [3], S. N. put forward a series of important suggestions, whose basic ideas recur through all the succeeding work: "The course of a reaction depends not only on radicals, but also on their interaction, on the dehydrating agent and on the conditions of the dehydration." As early as this article, he already states that "lability cannot be examined as a characteristic, independent value." He proved that the substance obtained earlier by Garder by treating phenylhydrobenzoin with HCl or HBr in an acetic acid solution and taken to be triphenylethylene oxide, was actually triphenylacetaldehyde [1, 3], while the substance obtained by Iakubovich by dehydrating allylhydrobenzoin, and considered by him to be the bimolecular full ether, was allyldiphenylacetaldehyde [4, 6] and S. N. not only established the structure of these substances, but also found conditions for the formation of either trisubstituted aldehydes or ketones during the rearrangement; he showed that triphenylacetaldehyde was obtained under more mild conditions and phenyldesoxybenzoin, under more drastic conditions and that under more drastic conditions, triphenylacetaldehyde was converted to phenyldesoxybenzoin [1, 3].



The aldehyde-ketone rearrangement, found for the aldehyde with a tertiary group, was then carried out in a series of works by S. N. and E. D. Venus-Danilova with other aldehydes, containing not only tertiary, but also secondary groups. It was found that isomerization may be induced by various acidic catalysts, dilute H_2SO_4 or a mixture of hydrochloric and acetic acid, and by mercury salts [8, 9, 11-14, 17, 18]. Similar reactions were soon noted in papers by M. Tiffen and A. P. Orekhov. Reaction with PCl_5 resulted in partial isomerization [4].

The discovery of the isomeric conversion of aldehydes to ketones – the Danilov aldehyde-ketone rearrangement – was of prime importance as it made it possible to examine more thoroughly the problem of the effect of conditions on the direction of α-glycol molecular rearrangement under the effect of an acid catalyst. In a detailed paper [12] on the dehydration of cyclohexylhydrobenzoin (I), it was shown that the direction of the rearrangement and the relative amount of possible reaction products [diphenylcyclohexylacetaldehyde (II), cyclohexyldesoxybenzoin (III) and benzhydrylcyclohexyl ketone (IV)] depended greatly on the process conditions and catalyst used.



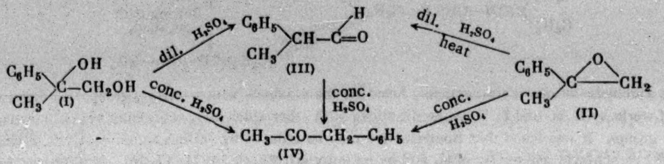
$$C_6H_5-\underset{C_6H_{11}}{C}OH-CHOH-C_6H_5 \rightarrow (C_6H_5)_2\overset{C_6H_{11}}{C}-C\overset{H}{\underset{O}{\lessgtr}} + \quad (I) \quad (II)$$

$$+\, C_6H_5-\overset{C_6H_{11}}{C}H-CO-C_6H_5 + (C_6H_5)_2CH-CO-C_6H_{11} \quad (III) \quad (IV)$$

Thus, the greatest aldehyde yield was obtained with oxalic acid; as the sulfuric acid concentration or the time of its effect increased the aldehyde and cyclohexyldesoxybenzoin contents decreased and that of benzhydryl cyclohexyl ketone increased; treatment with concentrated H_2SO_4 gave only the latter ketone. It is obvious from these data that the final result of the reaction does not depend on the structure of the original glycol but is determined by the conditions of the process. It was shown by separate experiments that treatment with conc. H_2SO_4 isomerized diphenylcyclohexylacetaldehyde (II) to benzhydryl cyclohexyl ketone (IV), i.e., to the ketone which is obtained as the sole product from the glycol under the same conditions.

In 1920 S. N. first put forward the idea that ketones, the same as aldehydes, could be converted to isomeric ketones; A. E. Favorskii and A. A. Chilingarian isomerized a ketone to another ketone, using as the example the conversion of isopropyl phenyl ketone to unsymmetrical methylphenylacetone; the ketone was isomerized by heating with $ZnCl_2$ at 350°, i.e., under considerably more drastic conditions than that used for α-glycol dehydration; in both cases, both with dehydration and isomerization, the processes terminated with the formation of the same ketone. Attempts to isomerize cyclohexyldesoxybenzoin to benzhydryl cyclohexyl ketone were unsuccessful. From this work, as well as from the data of earlier papers on the capacity of aldehydes to isomerize to ketones, S. N. came to the following conclusion: "if the dehydration product is a mixture of aldehyde and ketone, the ratio of the conponents in the given mixture may be changed by using more concentrated acid and greater heating" [12]. However, it did not follow from this that aldehydes always formed as intermediate products when α-glycols were treated with concentrated sulfuric acid; it could be assumed that conversion of α-glycols to ketones or aldehydes by treatment with concentrated sulfuric acid and, correspondingly with dilute sulfuric acid, proceeded by different mechanisms.

In order to find out whether any structurally stable substances – aldehydes, oxides or dioxane derivatives – form as intermediate products during the conversion of the α-glycol to the ketone, it is necessary to study the interrelations of all these compounds under the reaction conditions and the possibility of their interconversion. S. N. and E. D. Venus-Danilova undertook such an investigation by studying the interrelation between unsymmetrical methylphenylethylene glycol (I) and the anhydride forms corresponding to it – oxide (II), the full ether of the glycol as well as methylphenylacetaldehyde (III) and methyl benzyl ketones (IV) [18]. Treatment of the α-glycol with mineral acids gave, as in other cases, different carbonyl-containing compounds, depending on the conditions, and under drastic conditions the aldehyde was converted to the ketone. The oxide behaved similarly. All the conversions may be represented by the following diagram.



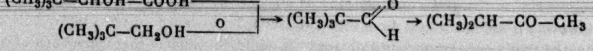
The oxide is hydrated completely to glycol in a weakly acid medium in the cold; however, with heating in a moderately acid medium both the oxide and the glycol give the full ether — a dioxane derivative. From the properties and behavior of the oxide and full ether in an acid medium under various conditions, S. N. and E. D. Venus-Danilova concluded that these anhydrides were not intermediate products; their presence among the reaction products indicates that the process proceeds simultaneously in different directions.

On the basis of his own experimental data and considering that aldehydes have greater heats of combustion than ketones, S. N. concluded that, in examining the factors affecting the direction of α-glycol conversions, it is necessary to take into consideration the energetics of the process, namely: the system of reacting substances tends towards conversion into the substances most stable at the given temperature, concentration of reagent, etc; if several substances with different stability may be formed under these conditions then step-wise conversion of the substances occurs in accordance with Ostwald's law. Similar considerations were put forward several times in A. E. Favorskii's papers.

Having rejected the idea that compounds with a definite chemical structure, genetically related to the starting glycol, are formed as intermediate products, S. N. assumed the formation in dilute acids of a different type of molecular (oxonium) compound, which has an extremely labile ("loose") bond between the reagent and glycol or its anhydride; according to S. N., in concentrated acids the complexes are more complicated and at first ethers are formed, as Meerwein had assumed. By this time it was established in Meerwein's work that an important factor determining the starting direction of the process with unsymmetrically substituted ethylene glycols is the different lability of the hydroxyls; according to S. N. it is determined by "acid-forming properties" of radicals, which could be evaluated by comparing the molecular electroconductivities of monobasic acids, which correspondingly have the same hydrocarbon groups [13, 18].

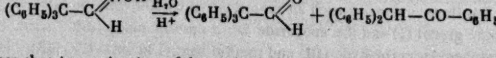
Thus, S. N.'s work describes a series of important circumstances which must be considered in interpreting the mechanism of the molecular rearrangement of α-glycols.

In concluding this section, one should note that on the basis of the aldehyde — ketone rearrangement discovered by S. N., certain observations described in the literature became comprehensible, such as the formation of methyl isopropyl ketone by heating trimethyllactic acid with 90% sulfuric acid and the formation of the same ketone by oxidizing 1,1,1-trimethylethanol; in both cases, according to S. N. [1, 3], under the reaction conditions isomerization of the aldehyde to ketone occurs by the scheme:



$$\left.\begin{array}{l}(CH_3)_3C{-}CHOH{-}COOH \xrightarrow{-HCOOH} \\ (CH_3)_3C{-}CH_2OH \xrightarrow{\quad O \quad} \end{array}\right] \rightarrow (CH_3)_3C{-}C\begin{smallmatrix}O\\H\end{smallmatrix} \rightarrow (CH_3)_2CH{-}CO{-}CH_3$$

S. N. Danilov and E. D. Venus-Danilova showed that in regenerating trisubstituted aldehydes from their derivatives in an acid medium, isomeric conversions may occur which limit the applicability of this method for the purification of this type of aldehyde [3, 8]. For example, hydrolysis of the oxime and semicarbazone of triphenylacetaldehyde gave a mixture of aldehyde and triphenylethanone [3].

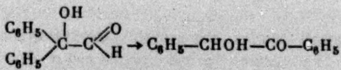


$$(C_6H_5)_3C{-}C\begin{smallmatrix}NOH\\H\end{smallmatrix} \xrightarrow[H^+]{H_2O} (C_6H_5)_3C{-}C\begin{smallmatrix}O\\H\end{smallmatrix} + (C_6H_5)_2CH{-}CO{-}C_6H_5$$

It was later shown that isomerization of di- and trisubstituted aldehydes to ketones may proceed also under conditions of heterogeneous catalysis; thus, trisubstituted aldehydes, catalyzed by aluminum sulfate at 320-350°, were isomerized to ketones [24]; these observations showed that care had to be taken in interpreting the experimental data on pyrolysis of natural products which occur in the presence of ash,as certain of its components may act similarly as catalysts; as a result, ketones, isolated from the reaction mixture, may be formed by the isomerization of the initially formed aldehydes.

In 1925 S. N. and E. D. Venus-Danilova started a systematic study of the behavior of α-hydroxyaldehydes under the action of various types of catalysts. The work on α-hydroxyaldehydes in an acid medium is a logical continuation of the work on the isomerization of aldehydes to ketones; in addition it is closely related to the work of A. E. Favorskii and co-workers on the isomerization of α-ketoalcohols in an acid medium.

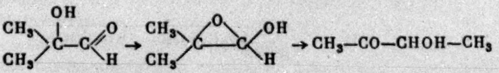
From the data given by Nef, who obtained acetyl- and benzoylcarbinols by hydrolyzing the acetals of lactic and mandelic acids, it was concluded that the simplest α-hydroxyaldehydes, which are isomerized to α-ketoalcohols with the transfer of two hydrogen atoms, are very labile. Therefore, it was most interesting to isomerize α-hydroxyaldehydes with a tertiary alcohol group,as in this case the rearrangement of the carbon skeleton of the molecule should occur. S. N. discovered hydroxyaldehyde – hydroxyketone isomerization on the example of the conversion of diphenylglycolaldehyde to benzoin by heating at 130-140° in an alcohol solution in the presence of a few drops of conc. H_2SO_4 [20].



$$(C_6H_5)_2C(OH)-CHO \rightarrow C_6H_5-CHOH-CO-C_6H_5$$

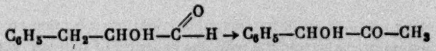
Thus, essentially, S.N. Danilov discovered a new form of isomeric conversion. Partial isomerization of diphenylglycolaldehyde also occurs when it is heated in an alkaline solution of copper hydroxide or an alcohol solution of mercuric chloride. In this case there is a considerable amount of benzil among the oxidation products of the hydroxyaldehyde. Later on α-hydroxyisobutyraldehyde and dicyclohexylglycolaldehyde were isomerized similarly [21, 22].

According to S. N. Danilov and E. D. Venus-Danilova, hydroxyaldehyde – hydroxyketone rearrangement in an acid medium proceeds with the intermediate formation of α-hydroxy oxides.



The same type of mechanism was proposed by A. E. Favorskii for the isomeric conversion of α-ketoalcohols in an acid medium. Quite recently, the hypothesis on the intermediate formation of α-hydroxy oxides was confirmed by the work of T. I. Temnikova and E. N. Kropacheva, using the isomerization of α-methoxy oxides as an example; however, taking into account the catalytic effect of sulfuric acid on these conversions, one should consider the participation of the proton, coordinately bound to the oxygen atom. It is possible that a similar scheme is also applicable to catalysis with metal salts that are capable of complex formation. S. N. proposed a mechanism for processes catalyzed by alkali solutions of cupric oxide, which is similar to the mechanism of other oxidation-reduction reactions (the reactions of Cannizzaro, V. E. Tishchenko and Meerwein and Pondorff).

The next stage in S. N.'s work was the study of the stability of α-hydroxyaldehydes, which have a secondary alcohol group and are homologs of the extremely labile, simplest α-hydroxyaldehydes, that is mandelo- and lactaldehyde. He found that secondary α-hydroxyaldehydes in an alcohol – sulfuric acid medium were more completely isomerized: instead of the expected primary α-ketoalcohol, benzylglycolaldehyde gave phenylacetylcarbinol [29].



$$C_6H_5-CH_2-CHOH-\overset{\overset{O}{\|}}{C}-H \rightarrow C_6H_5-CHOH-CO-CH_3$$

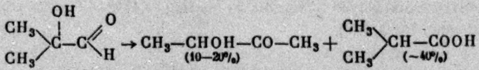
A similar conversion was observed later by E. D. Venus-Danilova and V. F. Kazimirova, who obtained methylacetylcarbinol by isomerizing α-hydroxybutyraldehyde.

In order to establish the mechanism of these interesting rearrangements which could not be explained by alcohol-oxide schemes, it was necessary to find out whether α-ketoalcohols, containing a primary alcohol group, were converted to isomeric α-ketoalcohols with a secondary alcohol group with the position of the carbonyl unchanged (1,3-rearrangement), for example

$$C_6H_5—CH_2—CO—CH_2OH \rightarrow C_6H_5—CHOH—CO—CH_3$$

The formation of primary α-ketoalcohols from α-hydroxyaldehydes is quite probable as this type of conversion is well known for monosaccharides (epimerization). However, S. N. Danilov and N. S. Tikhomirova-Sidorova established that the primary α-ketoalcohols, $C_6H_5CH_2CO-CH_2OH$ and $CH_3CH_2-CO-CH_2OH$, are not isomerized under the conditions used for conversion of hydroxyaldehydes to secondary α-ketoalcohols [94]. Thus, the mechanism of the deep isomerization of secondary α-hydroxyaldehydes remains unexplained.

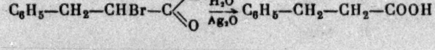
α-Hydroxyisobutyraldehyde is only partially isomerized to a hydroxyketone in the presence of an alkali solution of copper hydroxide. The main product is isobutyric acid which is formed as a result of an isomeric acid conversion [34]; this type of rearrangement, similar to the saccharinic rearrangement, is well known for monosaccharides.



$$(CH_3)_2C(OH)—CHO \rightarrow \underset{(10-20\%)}{CH_3—CHOH—CO—CH_3} + \underset{(\sim 40\%)}{(CH_3)_2CH—COOH}$$

Without cupric oxide in the alkali medium, the α-hydroxyaldehydes, in contrast to a monosaccharide, are converted by Cannizzaro's reaction to a mixture of α-hydroxyacids and α-glycols. Only α-hydroxyaldehydes with a tertiary hydroxyl are capable of acid conversion.

The work on isomeric conversions of α-hydroxyaldehydes to α-hydroxyketones or to saturated acids is closely connected with S. N.'s investigations in the field of α-haloaldehydes in the presence of alkali solutions of heavy metal hydroxides. Haloaldehyde conversions are similar to those of α-hydroxyaldehydes, which are related to them genetically. In many cases, hydroxyaldehydes and bromoaldehydes were investigated in parallel. Using α-bromodicyclohexylacetaldehyde and α-bromobenzylacetaldehyde as examples, S. N. Danilov and E. D. Venus-Danilova demonstrated the possibility of almost quantitative conversion of bromoaldehydes to saturated acids by heating them with water and silver oxide [23, 29].



$$C_6H_5—CH_2—CHBr—CHO \xrightarrow[Ag_2O]{H_2O} C_6H_5—CH_2—CH_2—COOH$$

These investigations, on the other hand, are the direct continuation and development of the work of A. E. Favorskii and co-workers on the acid conversion of haloketones.

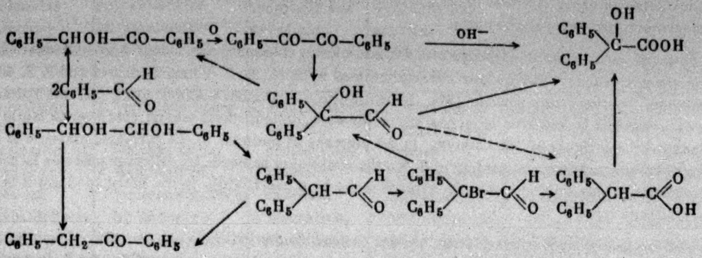
The mechanism of the conversions of haloaldehydes and haloketones to saturated acids are, most probably, similar. In this case, isomeric conversion does not occur, but substitution of the halogen atom by a hydroxyl, complicated by the rearrangement of the reacting molecule's skeleton. In such processes deeper changes in the skeleton may occur than in isomeric conversions. Thus, S. N. Danilov and N. S. Tikhomirova-Sidorova proved that extensive rearrangement may occur in replacing the chlorine in α-chloroketones by a hydroxyl [79]. Heating 1-chlorobutanone-2 with an alkali solution of potassium plumbite gave a mixture of propionyl- and methylacetylcarbinols.

$$CH_3—CH_2—CO—CH_2Cl \rightarrow CH_3—CH_2—CO—CH_2OH + CH_3—CHOH—CO—CH_3$$

As mentioned above, special experiments showed that primary alcohols are not converted to secondary ones [94].

All the isomeric conversions studied are intramolecular oxidation-reduction processes. It seemed interesting to apply the polarographic method to evaluating the reducing capacity of isomeric ketoalcohols and chloroketones. Comparison of the polarographic characteristics of 1-chloro- and 3-chlorobutanones-2 and those of the α-ketoalcohols corresponding to them, showed that the capacity for reduction of the primary chloroketone is less than that of the secondary; in the case of ketoalcohols the reverse is the case: methylacetylcarbinol is reduced more readily than propionylcarbinol [94].

The various types of isomeric conversions and molecular rearrangements studied by S. N. may be summarized by the following general scheme for the transitions of genetically interrelated substances; the scheme uses as an example compounds with two phenyl groups and two carbons in the chain and is completed by data from other authors.

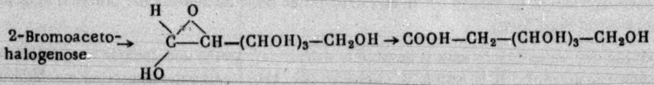


The types of conversion, first carried out by S. N. are shown by the darker arrows; isomerization of a hydroxyaldehyde, using diphenylglycolaldehyde as the example, was predicted (marked by dashes); a similar reaction was carried out using α-hydroxyisobutyraldehyde.

It is interesting to examine briefly the characteristics of the salt catalysts (heavy metal salts) that S. N. used widely in studying isomeric conversions. Salt catalysts and, in certain cases, concentrated sulfuric acid, have a double effect: on the one hand they form quite labile complex compounds with the starting materials and thus facilitate isomeric conversion; on the other hand, as they are more stably and complexly bound with the isomerized molecules, they stabilize the latter; as a result the position of the equilibrium is determined, not by the stability of the compounds themselves, but by the relative stability of the complexes with the catalyst. According to S. N., this is the reason for the formation of the same substances in different processes which use the same catalysts (for example, mercury salts) [101].

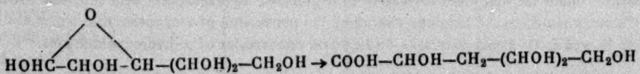
The numerous and varied works S. N. carried out in the field of monosaccharides and disaccharides was the logical continuation of his investigations on the isomeric conversions of α-hydroxycarbonyl compounds. Having carried out the acid conversion of α-bromoaldehydes and α-hydroxyaldehydes, S. N. put forward the hypothesis that a bromo-2-aldohexose may be converted to a desonic type of acid or, in other words, an orthosaccharinic acid [50, 52]. Formulas were derived for all the theoretically possible saccharinic acids on the assumption that in an alkaline medium, forms with ethylene oxide, propylene oxide and hexylene oxide rings are produced, which are in a definite equilibrium with the more stable forms, pyranose and furanose, and the less stable form with a free carbonyl group.

Desonic acids may be formed from halogen monosaccharides by the scheme:



$$\text{2-Bromoacetohalogenose} \rightarrow \underset{\text{HO}}{\overset{\text{H}\quad\text{O}}{\text{C}}}\text{—CH—(CHOH)}_3\text{—CH}_2\text{OH} \rightarrow \text{COOH—CH}_2\text{—(CHOH)}_3\text{—CH}_2\text{OH}$$

Other saccharinic acids with an unbranched carbon skeleton and a methylene group, which are called stereoisomers of metasaccharinic acid, may be formed by the scheme:



$$\text{HOH}\overset{\frown\,\text{O}\,\frown}{\text{C—CHOH—CH}}\text{—(CHOH)}_2\text{—CH}_2\text{OH} \rightarrow \text{COOH—CHOH—CH}_2\text{—(CHOH)}_2\text{—CH}_2\text{OH}$$

The formation of other saccharinic acids may be represented similarly. S. N. considered that acids with branched skeletons formed from ketoses.

Under the conditions for isomerizing α-bromoaldehydes and α-hydroxyaldehydes (α-hydroxyisobutyraldehyde and others) to acids, S. N. and A. M. Gachokidze obtained glucodesonic acid from 2-bromotriacetylglucose by heating it with lead oxide and trimethylglucodesonic acid from bromotrimethylglucose [50, 52]. This reaction was later studied by A. M. Gachokidze using as examples galactoses, L-arabinoses, D-xyloses, D-arabinoses, lactoses, cellobioses and maltoses.

The development of the synthesis of orthosaccharinic acids is a valuable contribution in the field of molecular rearrangements and to sugar chemistry.

The epimeric conversions of carbohydrates are also closely related to the isomeric conversions of hydroxycarbonyl compounds. Glucose and fructose were epimerized by S. N., E. D. Venus-Danilova and P. S. Shantarovich, by a new method: heating in dry pyridine [27]. In contrast to the previous methods using mineral hydroxides, under the new conditions no mannose or saccharinic acids were formed; there was no cleavage to lactic acid which indicates the specificity of the catalyst. In the presence of moisture in the pyridine, mannose is formed in the glucose-fructose mixture. According to S. N., the conversion proceeds by different schemes in the dry and in water-containing media as in one case the catalyst is the base itself, while in the moist medium it is a hydroxide of the ammonia type.

The new method of sugar epimerization, besides definite theoretical interest, was also of practical importance as it was widely used for the synthesis of previously unknown ketopentoses. This also fully confirmed S. N.'s conclusion on the specificity of the catalyst's effect. For example, Schmidt and Treiber prepared D-xyulose without traces of altrose by heating D-xylose in dry pyridine. The investigations of Vargha, Levene and Hill also confirmed these data and conclusions. S. N. explained monosaccharide epimerization by the transposition of hydrogen and hydroxyl between the first and second carbon atoms with the help of catalysts.

In works by S. N. and P. T. Pastukhov [71, 73], it was shown that heating of maltose and cellobiose with pyridine did not induce the epimerization of these disaccharides to ketobioses; only anomeric conversion of the α- and β-forms occurred. However, in the presence of small amounts of lime the cellobiose gave β-(1,5)-D-glucosido-4-(1,5)-D-mannose. Cleavage of cellobiose to methylglyoxal was observed in more concentrated alkali solutions. In work on the acetolysis of cellulose [73], the conditions for obtaining the greatest yields of cellobiose were developed. The role of temperature, time, conposition of the acetolysis mixture, water content of the cotton material and the amount and nature of the catalyst were clarified. The advantages of perchloric acid in comparison with sulfuric acid were shown. The former does not form esters with cellulose or its cleavage products and gives better yields of cellobiose octaacetate. The problem of designating α- and β-forms as cis- and trans-isomers was examined in the work. Being of practical importance, as it described the preparation of cellobiose under efficient conditions, this work also clarified the mechanism of acetolysis; namely, in cellulose acetolysis, acetic anhydride (acetic acid) is added by the links, binding the monosaccharide residues, and as a result these bonds are broken, while under these conditions the internal monosaccharide links are stable.

The problem of the configuration and reactivity of sugar anomers was examined in the work by S. N. and O. P. Koz'mina [105]. In studying the effect of phosphorus pentachloride on sugar the German chemist Brigl concluded that this reaction did not occur with high-melting cellobiose octaacetate or with α-glucose. Actually, the reaction occurs with α- and with β-form of sugar acetates but with different yields of the most stable tetrachloride. The investigations S. N. carried out in this field define more accurately the problem of the reactivity of various stereoisomeric sugar forms.

A considerable section of S. N.'s work is devoted to anhydrides, amino and guanido derivatives of carbohydrates and polyhydric alcohols. S. N. and L. S. Lishanskii [89, 100] studied the formation mechanism of α-oxides and the introduction of ammonia, methylamine and guanidine into a sugar molecule through an α-oxide ring. These investigations are valuable in the synthesis of streptomycin, which contains in its molecule a guanido derivative of inositol and a methylamino derivative of L-glucose. In connection with this, one should note that the American chemists Wolfram and Lemieux examined the conversion of a streptomycin molecule on the basis of the work by S. N. and E. D. Venus-Danilova on isomeric conversions of α-hydroxyaldehydes.

In order to find the best method for introducing a guanido group into monosaccharides, experiments were carried out in different directions including a study of the effect of S-methylisothiourea and O-methylisourea on 2-desoxy-2-amino-4,6-benzylidene-α-methylaltroside and 1,2-isopropylidene-6-desoxy-6-aminoglucose. This gave results which allowed a critical evaluation of the existing methods of guanidation and showed that the deciding factor in the reaction of S-methylisothiourea with the amine was the degree of basicity of the amine — the higher the basicity the more readily the guanidation proceeded.

TABLE

Simultaneous Oxidation-Reduction Reactions in the Carbohydrate Group and their Conversion Products

Intramolecular oxidation-reduction		Intermolecular oxidation-reduction			
monomolecular intramolecular oxidation-reduction I	polymolecular intramolecular oxidation-reduction II	hydrolytic and solvolytic cleavage III	hydration and alkaline oxidation-reduction IV	dehydration and decarboxylation oxidation-reduction V	desoxidation of carbohydrates VI
1. Tautomerism (enediols). 2. Isomerization of aldehydes and ketones and hydroxyaldehydes and hydroxyketones into hydroxyketones. 3. Epimerization of monosaccharides, Amadori rerrangement. 4. Saccharinic rearrangement: a) of monohydroxyaldehydes (hydroxyisobutyraldehyde into isobutyric acid), b) of monosaccharides c) of monohaloaldehydes, haloketones and halomonosaccharides. 5. Isomerization of triose to lactic acid. 6. Conversions (inter) of aldehydes, pyranose and furanose forms, anomers. 7. Synthesis of inositol from hexoses (transfer of a hydrogen atom and cyclization of a biradical).	1. Hydrogen bonds (cellulose and nucleic acids). 2. Synthesis of monosaccharides by Butlerov's method, synthesis of oligosaccharides. 3. Polymerization of formaldehyde and α-oxides of glycidic alcohol. 4. Conversion of hexose into trioses and back. 5. Acyloin, benzoin, aldol and complex ether condensation of aldehydes.	1. Hydrolysis of oligosaccharides and polysaccharides. 2. Acetolysis, alcoholysis and mercaptolysis of polysaccharides.	1. Hydration of glucal into a desose 2. Hydration of anhydrosugars and anhydrides of polyhydric alcohols. 3. Cannizzaro reaction for aldehydes, hydroxyaldehydes and monosaccharides. 4. Benzil rearrangement. 5. Amination and guanidation of sugars.	1. Anhydrization of monosaccharides, disaccharides and polyatomic alcohols. 2. Anhydrides of cellulose (anhydrocellulose). 3. Formation of methylglyoxal from monosaccharides. 4. Decarboxylation (pyruvic acid) 5. Hydroxymethylfurfural, methylfurfural, furfural and maltol from carbohydrates.	1. Formation of methyloses and methylpentosans and desoses. 2. Desoxycellulose 3. Celluloseens and glucoseens. 4. Levulinic acid from hexoses (complex conversion). 5. Aromatization of carbohydrates (polyphenols).

From the experimental data the authors concluded that the guanidation mechanism proposed in the literature was incorrect. The effective initiator in guanidation is apparently cyanamide at the moment of evolution. It was then established that the action of alcoholic guanidine solutions on monosaccharide anhydrides at 100° is similar to the action of alkali metal alcoholates, i.e., an alcohol molecule is added by the oxide ring and no guanido derivative is formed. The authors considered that guanidine formed a molecular compound with alcohol and this was also confirmed by reacting monoacetylguanidine with the same anhydride (2,3-anhydro-4,6-benzylidene-α-methylalloside) in an alcohol solution. The main product was the same 2-methyl-4,6-benzylidene-α-methylaltroside, as in the first case. Under the experimental conditions guanidine hydrochloride was dissociated in an alcohol medium and the hydrogen chloride ruptured the anhydride ring to form 3-chloromonosaccharides. A different method was used for introducing the guanido group: the monosaccharide anhydride was heated in a pyridine solution of guanidine. Thus, a new, simple and convenient method for synthesizing carbohydrate guanido derivatives was demonstrated.

The work confirmed the rule that a trans-position of the adjacent hydroxyls is required for the formation of anhydro rings in sugars. There are several explanations for the need for a trans-configuration. S. N. Danilov gave one of the most probable explanations. He considers that the first stage in anhydro formation, under the action of alcoholates,is the addition of alcoholate to the free hydroxyl group. In the case of a cis-configuration this addition is greatly hindered by the effect (either electronegatively or simple-sterically) of the tosyl group. With a trans-configuration this phenomenon is much weaker. The alcoholate addition product formed then decomposes to give salts of the sulfonic acid and form the anhydride; inversion of the carbon atom, which bore the tosyl group, occurs. On the basis of experimental material and by generalizing literature data, S. N. put forward a general hypothesis on the factors affecting the direction of oxide ring rupture in monosaccharides and polyhydric alcohols, which he propounded in a report to the Kiev Conference on Problems of the Mechanism of Organic Reactions [93]. S. N. noted that the direction of rupture of the oxide ring is affected by: a) the position of the oxide ring relative to the plane of the pyran ring of the whole molecule, b) the α- or β-configuration of the first carbon atom and substituent on it and c) the character and position of other substitutents in the molecule. These basic premises were confirmed by a series of experimental and literature facts.

Other investigations by S. N. et al. lead to the synthesis of a series of new derivatives of polyhydric alcohols and their anhydrides and monosaccharides. The chlorohydrin of 1,4-anhydroxylitol, which was first prepared by S. N. and V. F. Kazimirova [92], was the starting material for new derivatives. In the Institute of High-Molecular Compounds of the Acad. Sci. USSR, S. N. et al. [107] started from xylitol, xylitan and xylitan chlorohydrin and obtained their acetals, ketals, urethans, unsaturated ethers, amino derivatives and other compounds, which in their turn act as intermediates for the synthesis of new substances in the chemistry of high-molecular compounds.

In a brief summary one should note , in at least a few words, the work by S. N. and L. I. Rastorgueva [99] in which they developed a method of hydrolyzing alginic acid and obtained a series of new derivatives of mannuronic acid. This work showed that, as is generally the case with polysaccharides, the products of alginic acid hydrolysis offer many possibilities for the synthesis of practically valuable substances in the difficult and interesting field of sugars and polyhydric alcohols.

In his numerous reports and lectures S. N. examined the conversion of oxygen-containing organic compounds as a simultaneous oxidation-reduction reaction. In 1949 [87] he put forward a strict classification of the oxidation-reduction reactions, having systematized and expanded them to cover many groups of compounds. Later [112] this classification was developed in greater detail, especially for hydroxycarbonyl compounds and carbohydrates, including cellulose, and this is shown in the table. Many of the types of oxidation-reduction reactions given in the table were carried out by S. N. et al. ($I_{2,3,4}$; $III_{1,2}$; IV_5; $V_{1,2,3}$; $VI_{2,3}$).

From the point of view of intramolecular oxidation-reduction, S. N. examined many biochemical reactions and, for example, explained the ripening of the product of glucose epimerization to the sweeter fructose [112].

The well-known reactions of carbonyl and hydroxycarbonyl compounds, carbohydrates and polyhydric alcohols discovered by S. N. Danilov open up many interesting directions and will be the object of new and numerous investigations in organic chemistry and the chemistry of high-molecular compounds.

THE WORKS OF S. N. DANILOV IN THE FIELD OF CELLULOSE AND ITS ETHERS AND ESTERS

E. A. Plisko, M. G. Okun', N. M. Grad and N. F. Gintse

The many-sided scientific activity of S. N. Danilov is closely connected with problems in the study of the chemistry of cellulose and its derivatives and also of alginic acid and chitin. New data were obtained on the behavior of cellulose towards solvents, on nitrocellulose, acetylcellulose and nitroacetylcellulose, on cellulose ethers and on the hydrolysis of alginic acid and the information on chitin extended.

These works were developed in the early 30s in the laboratory of the Lensoviet Technological Institute, Leningrad (L.T. I.) and lately, investigations are being carried out on other polysaccharides, as well as cellulose, in the High-Molecular Compound Institute of the Acad. Sci. USSR.

In joint work, S. N. and N. F. Gintse studied the effect of various conditions on the solubility of cellulose in phosphoric acid [104] and found that the solubility curve of cellulose in strong phosphoric acid relative to acid concentration had two maxima, corresponding to regions of unlimited swelling with an intermediate region of incomplete solubility between them. The positions of the maxima corresponded to those acid concentrations at which the acid existed in the form of a monohydrate and a polyhydrate. These facts indicate the essential role of hydrates in the solution of cellulose in concentrated electrolyte solutions. Preliminary activation of the cellulose with water or dilute phosphoric acid made it possible to achieve complete solution of the cellulose material along the whole length of the curve, including the intermediate region between the maxima.

The role and the effect of hydrates was reported in another work by S. N. et al. on the study of the properties and vapor pressure of nitric acid in phosphoric-nitric acid mixtures [68]. In these mixtures, the course of the vapor pressure-composition curves is conditioned by the decomposition of nitric acid hydrates in the presence of phosphoric acid. The dehydrating effect of phosphoric acid appears only as a strong retardation of the fall in nitric acid vapor pressure, while for mixtures of sulfuric acid nitric acids and water, over a certain range of concentrations there is an increase in pressure to a maximum and a subsequent fall, which is explained by the stability of the monohydrates and even the dihydrates of sulfuric acid. Phosphoric acid was shown to contain a stable hydrate only with a content of 1 molecule of water to two molecules of phosphoric acid, $2H_3PO_4 \cdot H_2O$.

A study of the softening of viscose films (cellophane) with aqueous solutions of glycerol [75] showed that as the concentration of the softening baths increased, the difference between the composition of the solution, held by the film, and the composition of the softening bath decreased and with a softening bath with 65% concentration, this difference disappeared completely, i.e., the film began to absorb the contents of the bath with constant composition. These data on the absorption by a cellulose film of an aqueous glycerol solution of constant composition at a solution concentration of about 65%, at which the glycerol hydrate of composition $C_3H_8O_3 \cdot 3H_2O$, found by D. I. Mendeleev in aqueous solutions of glycerol, exists, indicates the significance in absorption of molecular compounds in solution.

Mention should be made of the work of S. N. and N. F. Gintse [74] on the thermal insulation materials of low specific gravity, obtained by mixing cellulose with phosphoric acid and a gas-forming substance. An examination was made of the effect of phosphoric acid concentration, solution time, and solution and precipitation temperature on the volumetric weight and the shrinkage of the mass. Increasing the acid concentration makes it possible to increase the cellulose concentration, which leads to the production of a composition of better forming properties and with a lower specific volume due to an increase in the amount of gas-former, while a very uniform and fine porosity is obtained. The use of 95-96% phosphoric acid without a frothing agent gives a composition with a volumetric weight of 0.15-0.20, while a cellulose concentration of 8-9% is achieved under laboratory conditions and in work on an experimental apparatus with stone rollers, a cellulose concentration of 11-12% is convenient. All operations were performed at a temperature of about 10°.

One of the most important characteristics of cellulose in the production of cellulose ethers and esters or in the preparation of hydrate fibers is the copper number. The copper number is usually determined under heterogeneous conditions, which is suitable for cellulose fiber, but is not applicable to regenerated, compressed fibers, since under these circumstances the normal method gives low results. S. N. and O. P. Koz'mina [67] developed a method of determining copper numbers under homogeneous conditions in Schweitzer's solution.

Interesting data were obtained on the preparation and study of the properties of modified cellulose molecules, impoverished by one oxygen atom. Investigations were made on developing syntheses and studying the properties of desoxy, anhydro and unsaturated derivatives of cellulose. In joint work with A. A. Lopatenok, S. N. examined conversions of cellulose ethers using the P. P. Shorygin reaction (cleavage with sodium in liquid ammonia) with the aim of preparing desoxy derivatives of cellulose. The best results were obtained with cyanoethyl ethers of cellulose. In the cleavage of cyanoethyl cellulose with sodium in liquid ammonia, the cyanoethyl residues were removed completely, mainly to give hydroxyl groups and partly to give desoxy groups (0.45 groups per glucose residue). In the cleavage of p-toluenesulfonic groups with metallic sodium in liquid ammonia, anhydro derivatives of cellulose were obtained and these could also be obtained by the action of organic bases on p-toluenesulfonic esters of cellulose.

Together with a study of the chemistry of cellulose, the synthesis conditions of cellulose ethers and esters and the mechanism of nitration and transesterification, S. N. made a thorough study of the colloidal chemical properties of cellulose derivatives under processing conditions. Mineral impurities were found to have a great effect on the colloidal chemical properties. In an investigation of acetylcellulose, S. N. et al. [62] established that mineral impurities in acetylcellulose were the reason for the anomalous viscosity and the increased viscosity of its solutions. In contrast to other calcium salts, the presence of calcium acetate in acetylcellulose solution increased the viscosity of acetylcellulose lacquer so much that it could not be determined. To determine the relation between the structural viscosity and the mineral impurity content, investigations were made with dilute solutions to show the effect of structurality, which depends only on the mineral impurities.

S. N. and R. S. Aleksandrova [48] found that for benzylcellulose there was a deviation from the Khagen – Poiseuille law in concentrated solutions and the viscosity was not anomalous in dilute solutions (to 2%). The effect of the solvent on the deviation from Poiseuille's law was established. The viscosity and solubility of ethyl cellulose [46] depended on the nature of the ether, the degree of substitution and the method of treatment and on the viscosity of the liquid components forming the system. It was found that the best solvents, in which clear films with good mechanical and other indexes were obtained, were mixtures of benzene and toluene with alcohol.

In the laboratory of L.T.I. and the Institute of Agrophysics, under the direction of Academician A. F. Ioffe, a large amount of material was obtained on the use of acetylcellulose films instead of glass in hotbeds, since such films will transmit ultraviolet rays well.

In a series of works, a detailed study was made of nitric esters of cellulose and the action of weak and strong bases [43] and acetic acid [76] on nitrocellulose was examined. The reasons for the reduction in the viscosity of nitrocellulose by ammonia was studied [36]. It was shown that in the treatment of nitrocellulose with substances of a basic character, there occurred a partial denitration, accompanied by oxidation of the nitrocellulose, producing fractions, which differed in solubility in alcohol. Such bases as ammonia and pyridine lowered viscosity more strongly than equivalent amounts of strong bases.

In the acetylation of nitrocellulose with acetic acid, it was established that together with the introduction of acetyl groups into the product, there was also a fall in the nitrogen content. Increasing the reaction temperature accelerated the fall in nitrogen, but the total degree of esterification of the cellulose derivatives obtained remained constant. Consequently, the mechanism of the acetylation of nitrocellulose with acetic acid consists of the substitution of nitro groups by acetyl groups.

Like other cellulose esters, nitrocellulose is solvated by solvents and swells in them either to a limited or an unlimited extent. The intensity of the reaction of the solvent with nitrocellulose may be characterized by the swelling pressure. S. N. and M. E. Dyn'kin [70] constructed an original apparatus to determine the swelling pressure and the work of swelling changed regularly in relation to the nitrogen content of the nitrocellulose and the composition of the solvent, but did not depend on the viscosity of the nitrocellulose. The swelling pressure and the work of swelling made it possible to compare the relative strength of interaction of the different nitrocelluloses with different solvents. With an increase in the degree of nitration, the swelling pressure decreased and there was an increase in the relative and structural viscosities of dilute solutions and in the pressures for squeezing and drying (elimination of solvent from concentrated systems and gels).

An outstanding investigation by S. N. on the mechanism of cellulose nitration confirmed and developed the theory of nitration of Mendeleev and Sapozhnikov. S. N. et al. [68], on the basis of the hydrate theory of Mendeleev and a study of the changes in the physicochemical indexes (vapor pressure, density, electrical conductivity, etc.) with composition of nitration mixtures, established the best conditions for the preparation of highly nitrated nitrocellulose by the action of phosphoric-nitric acid mixtures and showed the determining role of hydration and dehydration of the acids. The swelling of the cellulose is of great importance in the course of nitration. There is a definite linear relation between the degree of nitration and the degree of swelling in mixtures with a low water content. In the case of mixtures with a lot of water or a high nitrogen content swelling is considerable and, with excess nitric acid, the nitration process approaches permutoid reaction*.

The first hydroxybutyl ethers of cellulose were prepared [51] with various degrees of substitution, depending on the reaction conditions, and the maximum degree of substitution was obtained with longer heating times (up to 12 hours) and excess pseudobutylene oxide (up to 10 moles). In contrast to hydroxyethyl ethers of cellulose, which are readily soluble in water, hydroxybutyl ethers of cellulose, even with a high degree of substitution, were difficultly soluble in water due to the complexity of the substituent, but readily soluble in dilute alkali solutions to form extremely viscous solutions. More strongly hydrophilic properties were possessed by glycerol ethers of cellulose, as confirmed by experiment. S. N. et al. [66] obtained new data on the synthesis and the properties of glycerol ethers of cellulose. An examination was made of the action of monochlorohydrin, glycerol epichlorohydrin and glycidic alcohol on alkali cellulose and the effect of impurities on the properties of the glycerol ethers of cellulose obtained was demonstrated. The presence of traces of glycerol dichlorohydrin led to the formation of cross-linked molecules, which sharply changed the solubility of the ethers obtained in hydrophilic solvents. In contrast to the experiments of P. P. Shorygin, S. N. [66] was able to obtain readily soluble glycerol ethers of cellulose after careful purification of glycidic alcohol by repeated distillation.

In the nitration of glycerol ethers of cellulose, obtained using glycerol epichlorohydrin and glycidic alcohol, with nitration mixtures of various compositions, the effect of the nitration mixture composition on the degree of nitration was demonstrated and also the effect of the degree of etherification of the glycerol ethers on the nitrogen content of the nitro product was elucidated. Nitroglycerol ethers of cellulose from glycidic alcohol were considerably more soluble in ketones and esters than ethers obtained through epichlorohydrin.

S. N. Danilov and O. P. Koz'mina [78] studied the oxidative polymerization of allylcellulose and showed that under the action of heat and light, there occurred the addition of oxygen to allyl cellulose with subsequent decomposition of the oxidized molecule at the double bond to eliminate formaldehyde and form a three-membered structure by cross-linking of the ether-cellulose units. Oxidative polymerization also occurred under the action of peroxide compounds. In the absence of oxygen, allyl cellulose was not polymerized. The chlorination of allyl cellulose gave a chloro substituted allyl ether of cellulose, which was readily converted into an unsaturated chloride by the elimination of hydrogen chloride. Under the action of external conditions, the unsaturated chloride in its turn rapidly polymerized to form a chlorine-containing polymer of the chloroprene type.

Among the works of S. N. on the synthesis and study of the properties of hydrophilic ethers of cellulose, is the work on the preparation of carboxymethylcellulose [35]. An examination was made of the synthesis conditions, the effect of alkali concentration and reaction temperature and also the optimal molar ratios of the components, which affect the yield and degree of substitution, were found. Carboxymethylcellulose, which has extremely valuable properties, has found wide application in a series of fields. At the present time carboxymethylcellulose is produced in our factories and widely used in oil-well drilling, as a detergent, as a suspension thickener in printing, etc.

Many ethers of cellulose have been known for a long time, but investigations were not made from the point of view of the chemistry of the interaction of cellulose with alkali in reactions for the preparation of cellulose ethers. The question was whether the reaction proceeded through the alcoholate form or by means of a type of molecular compound. Using the simple models of plasticizer synthesis (benzyl ethers of ethylene glycol and glycerol), S. N. et al. [41] examined the synthesis of benzyl cellulose and showed that there was complete analogy between the formation of benzyl ethers of cellulose and the etherification of di- and trihydric alcohols, with the exception of the fact that the etherification of cellulose was a heterogeneous process. S. N. developed a rapid method of analyzing benzyl ethers of cellulose for factory control [40]. The method was based on the reduction of the thermal decomposition products of benzyl cellulose at the moment of their formation with hydrogen, formed by reacting aluminum or zinc with solid alkali. The thermal decomposition products of benzyl cellulose, containing the benzoxyl group $C_6H_5CH_2O$, were reduced to toluene. This method was also convenient for the analysis of mixed ethers such as ethylbenzyl cellulose and butylbenzyl cellulose.

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* Presumably meaning similar to a reaction with permutite – Translator's note.

S. N. made a considerable contribution to the science of natural polymers by his studies on chitin. In contrast to cellulose, chitin swells very little in alkalis and, therefore, will hardly undergo etherification. Conditions were found for activating chitin and under appropriate conditions, it was possible to dissolve chitin in alkali [96]. Glycerol ethers of chitin [97] were prepared for the first time by the action of glycerol monochlorohydrin or glycidic alcohol on alkali chitin. Due to traces of glycerol dichlorohydrin, the alklation of chitin with glycerol monochlorohydrin gave ethers which did not swell in water and alkali solutions and were even insoluble in concentrated solutions of hydrochloric and phosphoric acids. At the same time, glycerol ethers of chitin, obtained with glycidic alcohol, swelled in water and dissolved in dilute alkali solutions, depending on the degree of substitution. Of other hydrophilic ethers of chitin, the hydroxybutyl ether was prepared for the first time [111]. The optimal conditions were established for the preparation of water- and alkali-soluble ethers, which give viscous solutions in water and dilute acetic acid. There is practical interest in the ethyl ethers of chitin [111], which were prepared for the first time by S. N. and E. A. Plisko. These ethers dissolved in organic solvents forming viscous solutions, from which formed films, which were equal in mechanical properties to ethyl cellulose films. At present, work is proceeding on the preparation of carboxymethyl chitin and the study of its properties, a study is being made of the hydrolysis of chitin and a search is being made for methods of synthesizing other ethers for conversion to unknown anhydro- and desoxychitins.

The work of S. N. Danilov in the field of ethers and esters of cellulose is closely connected with his investigations in the field of cuprammonium solutions of cellulose, xanthates and viscose.

Over many years, S. N. has carried out a large amount of research work on determining the composition, the structure and the properties of cuprammonium compounds of cellulose and the factors affecting the preparation of cuprammonium spinning solutions. In the LTI Laboratory, S. N. investigated the preparation of basic copper salts and copper hydroxide [57], used in the production of cuprammonium fiber; methods for their analysis were developed simultaneously. It was found that, depending on the preparation conditions and the composition of the salts, they differed in the degree of dispersion and solubility in ammonia, which affected the solubility of cellulose and the properties of the spinning solution. Traces of salts, the presence of sulfate ion [58] and the addition of glucose [59] had a great effect on the properties of the solutions. These papers showed the necessity for careful control of the salts' composition in production and strict observation of the preparation conditions.

S. N. was one of the first to propose the method of coagulating a spinning solution by the addition of an electrolyte as a method of rapid control of the readiness of the solution. Under the direction of S. N., a detailed study was made of the effect of electrolytes on the solubility of basic salts and also the action of sulfite salts as agents to raise the viscosity of the solution and protect the cellulose from oxidation [60].

Stable spinning solutions are very difficult to obtain due to the ready oxidizability of the cuprammonium cellulose solution. For a number of years, S. N. has been investigating oxidation processes in cuprammonium cellulose solutions [69]. It was found that the main reason for retardation of oxidation in the presence of organic additives (tartaric acid, mannitol, glycerol, glucose and triethanolamine) was the increased viscosity of the solution due to the formation of compounds with the cuprammonium base by the organic polyhydroxy substances and, as a result, the separation of free copper from the solution. Mineral additives such as sodium sulfite and bisulfite are negative catalysts in the oxidation of cuprammonium solutions of cellulose. Sulfite and cellulose are oxidized very slowly as a conjugated reaction, when both are present in a cuprammonium solution, i.e., the cellulose and sulfite protect each other from oxidation. Here, the sulfite acts as an inhibitor, retarding oxidation [81]. In its turn, cellulose retards sulfite oxidation. Consequently, sulfite behaves not only as a substance which raises the viscosity of the solution and thus prevents it from oxidizing, but also as an agent which destroys the active centers in the substance being oxidized and the active oxygen atoms, thus breaking the oxidation chains at the beginning.

Under S. N.'s direction, extensive work on cuprammonium solutions of cellulose and other polyhydroxy compounds [98] was carried out by various physicochemical methods and this work solved certain problems in the chemistry of these solutions. Experiments with electrophoresis, ion exchange chromatography and spectrometry of the cuprammonium solutions of polyhydroxy compounds refuted the concept of the alcoholate nature of the copper-cellulose compound in the solution.

A direct study of the composition of the precipitates isolated from the cuprammonium solutions of cellulose under the action of salt and alkali solutions [103] indicated the absence from the precipitate of chemical compounds of constant composition, known in the literature as Normann compounds. As a result of these investigations, the cuprammonium solution of cellulose was found to be a molecular solution of a high-molecular substance $\{(C_6H_{10}O_5)_x \cdot [Cu(NH_3)_m(OH)_2]_y \cdot (H_2O)_z\}_n$, in which the cellulose formed with the cuprammonium base a molecular compound of variable composition, due to hydrogen bonds.

The beinning of S. N. Danilov's work in the field of xanthates and viscoses is connected with the organization in the USSR of the viscose artificial fiber industry. Many of S. N.'s works of this period are directly connected with problems of industrial technology. During these years S. N. wrote detailed reviews on the most important achievements of the time in the chemistry of xanthates, viscose and artificial fibers [115-117, 123]. It was then that the main directions of S. N.'s further experimental investigations in this field took shape.

The main series of works by S. N. on the chemistry of xanthates and viscose was devoted to a study of the chemical reactions of cellulose xanthates, viscose composition, in particular, the polysulfide compounds in ciscose that had been unknown previously, the role of separate components of viscose and additives, the complex processes of viscose ripening and the problem of carbon disulfide distribution in the main and side reactions in cellulose xanthation. S. N. and his co-workers found new data on the composition of viscose and its ripening procress, which resulted in the creation of a special section on the chemistry of viscose and in the formulation of new views on the processes occuring in viscose.

S. N. was the first to put forward the hypothesis that in the ripening of viscose, besides the hydrolytic processes, oxidation reactions also occur. It follows from S. N.'s work that in viscose solutions of cellulose there are, so to speak, model reactions of organic oxygen- and sulfur-containing substances, so that the oxidation in viscose may be divided into two large categories: 1) oxidation processes involving atmospheric oxygen, which affects the cellulose and other components of viscose solutions, and 2) oxidation and oxidation-reduction reactions of the sulfur-containing compounds in the viscose, which are capable of oxidation or donation and addition of sulfur [81]. The main works of S. N. on the chemistry of xanthates and viscose are devoted to the study of these two directions. Schemes for the oxidation reactions in viscose, proposed by S. N., are given in monographs and text books, describing the ripening processes of viscose.

Since 1934, the study of polysulfide compounds in viscose and their role in oxidation-reduction reactions is developed in S. N.'s work. The thioanhydride of cellulose xanthic acid was prepared for the first time by treating cellulose xanthate with benzoyl chloride [44]. Later on, first using models of simpler compounds (derivatives of ethyl ether, menthol and diacetoneglucose) and then using cellulose derivatives, it was shown that dixanthates were converted to thioanhydrides by the action of sulfur acceptors such as cyanides and sodium sulfide and sulfite [77, 85, 86]. The reactions of dixanthates of simple compounds (ethyl alcohol and the monobenzyl ether of ethylene glycol) and cellulose, when treated with sodium hydroxide and aniline, were studied in detail [72]. It was established that cellulose dixanthates do not differ in structure from the dixanthates of simple alcohols, which was questioned at one time by some authors (Berl' and Dilenius and Geiger).* It was shown [84] that during the oxidation of cellulose xanthate with oxygen, cellulose dixanthate was formed. Cellulose dixanthate was shown to be formed in viscose [84] under the action of atmospheric oxygen. It was established that the formation of dixanthates in viscose and their subsequent, inevitable decomposition in a strongly alkaline medium with the formation of xanthate with a lower degree of substitution and the accumulation of side products in the viscose [72], must accelerate the ripening of viscose. A study of the properties of thioanhydrides of cellulosexanthic acid [86] showed that due to the instability of the thioanhydride in alkali, it could not exist in viscose, although one cannot exclude the possibility of its formation in the ripening of viscose from cellulose dixanthate under the action of sulfur-abstracting substances, contained in viscose (sodium sulfide and sulfite). It was established that the side products in viscose included polysulfide compounds, such as sodium disulfide and perthiocarbonate, in addition to thiosulfate, which was known previously. This was proved both by indirect reactions with cyanide [55] and in subsequent investigations of viscose spectrographically. It was proved that polysulfide compounds accumulate in viscose as it ripens [85]. The mechanism of the action of sulfite in viscose, producing a more advantageous distribution of carbon disulfide, was elucidated [55].

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*Transliteration of Russian — Publisher's note.

Parallel with the study of the oxidative processes in viscose, a detailed study was made of the oxidative reactions and their inhibitors in alkali cellulose. This investigation was a most convenient example for a study of oxidative conversions of cellulose [84].

In papers devoted to elucidating the role of different components of viscose and its conversions, a study was made of the action of atmospheric oxygen, sulfur-abstracting substances and oxidation inhibitors on pure preparations of these components [84, 85]; the effect of alkali and salts on the decomposition rate of the xanthates of viscose was found [108]. An examination was made of the interaction of viscose components and the formation of sodium sulfide, as the initial substance forming trithiocarbonate, was noted.

During the investigations, S. N. and his co-workers developed new procedures and methods of analysis, including: the determination of the free carbon disulfide in viscose and xanthate [56], the determination of the degree of xanthation by means of chloroacetonitrile derivatives [67], analysis of viscose components in the form of cadmium [56] or zinc [108] salts, fractionation of xanthates with salt solutions [55] and the determination of polysulfide compounds by the cyanide method [85] in various ways, including the use of potentiometric titration. Tracer methods were used to determine the distribution of carbon disulfide in viscose between the components and to determine the sulfur donation of polysulfide compounds for the first time. See page 3221.

As has already been said, in a series of works, S. N. developed aspects—closely related to the technology of viscose production. In answer to the industrial problems in the development of the technology of producing viscose continuously, a study was made of the effect of various factors of the first stage of the process — mercerization — (increasing the temperature and changing the ratio of cellulose and alkali in the alkali cellulose) on the distribution of carbon disulfide in the xanthation between the main product (xanthate) and the side reactions [42]. Recently, it was shown to be possible to carry out a rapid emulsion xanthation with the production of a viscose with industrial characteristics. This xanthation was performed both with direct and reverse emulsions of carbon disulfide. The emulsions were obtained by the action of ultrasonics or by the use of the preparation OP-10 as an emulsifier [113].

As industry required an artificial fiber which could be dyed with wool dyes, a method was developed for rendering viscose wool-like with wool hydrolyzate. A series of works were carried out on the selection of the composition of precipitating baths. The physicochemical characteristics of the baths were described and it was shown that determination of the electroconductivity of the baths served as a good characteristic and indicated changes in the ionic balance during spinning [47]. The action of different salts on the decomposition and coagulation of viscose by baths was compared by an original method for separately studying the decomposing and coagulating action of baths [47, 61, 63] and equivalence coefficients were found for the main salt components of precipitating baths in relation to the slowing of the decomposing and the increase in the coagulating action of the baths [61]. The coefficients found were tested under actual conditions of spinning in a study on the action of various precipitating baths by an analysis of the filaments formed [63]. This showed the possibility of an efficient choice of the composition of precipitating baths on the basis of calculations and considerably extended previous attempts in this direction. A study was made of the conversions of sugars (hexoses and pentoses) in precipitating baths [53] and this was of particular interest as, in addition to the accumulation of hydrolysis products of the polysaccharides from the spun filaments in the bath, glucose was specially introduced into the baths for its softening effect, according to accepted recipes. The use of monosaccharides in the baths was shown to be unprofitable as the accumulation of sugars in the bath lead to the formation of gummy, lignin-like substances, which could produced inhomogeneous coloring of the fibers in textile treatment. The introduction of monohydric alcohols or hydroxyacids into the bath instead of monosaccharides was proposed.

Considerable work was done on the purification of exhausted alkalis from organic impurities with oxidizing agents [54], which have an effect on the practical purification of alkalis. A detailed investigation was made in laboratory experiments and on an experimental apparatus on the regeneration of products, emitted with factory flue gas, and also the problem of viscose production [64, 65]. Many valuable practical directions for the technology of viscose production were provided by the work of S. N. at LTI in cooperation with industry and presented in numerous reports.

This is a far-from-complete account of the problems and subjects which were and are being worked out under the direction of S. N. Danilov by his numerous students and colleagues, both in the field of the theoretical foundations of cellulose chemistry and in the field of the practical application of cellulose and its derivatives, as well as other high-molecular compounds.

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ANHYDRO, DESOXY AND UNSATURATED DERIVATIVES OF POLYSACCHARIDES

I. DESOXYCELLULOSE FROM CYANOETHOXYLCELLULOSE

S. N. Danilov and A. A. Lopatenok

Desoxidated monosaccharide derivatives, containing methylene groups instead of secondary alcohol groups (desoses) and methyl groups instead of primary alcohol groups (methyloses), occur in nature and may be synthesized by several methods. There are a few papers available on the preparation of desoxidated cellulose with the composition $(C_6H_{10}O_5-x)_n$, largely containing methyl groups and synthesized successively through the tosyl esters and iodo derivatives, mainly at the expense of primary alcohol groups.

Moreover, desoxidated celluloses were prepared by reduction [1, 2] either of iodo derivatives $(C_6H_{10-x}O_{5-x}I)_n$ directly or of unsaturated compounds (celluloseens), formed from iodo derivatives by elimination of hydrogen iodide.

A general method of preparing desoxidated celluloses with methylene and methyl groups was proposed by P. P. Shorygin on the basis of his reaction [3] of cleaving ethers with sodium alkyls [3] or metallic sodium [4], in particular in liquid ammonia.

Alkali metals in liquid ammonia remove acetyl groups from acetyl derivatives of sugars, forming alcoholates of the sugars [5, 6]. In the works of P. P. Shorygin and N. N. Makarova-Zemlianskaia (N. N. Shorygina), the cleavage of ethers with sodium in liquid ammonia was applied to methylated sugars [7, 8] and also to methyl cellulose [9], the benzyl ether of cellulose and acetylcellulose.

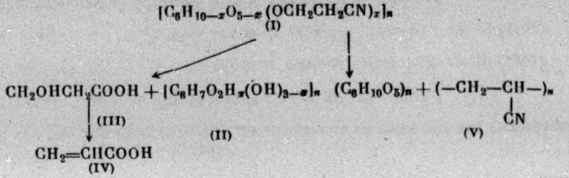
Desoxidation of cellulose was achieved in the case of methyl cellulose.

About 15% of the methoxyl groups, available in the methyl cellulose, were cleaved in the direction of desoxycellulose formation through the metalloorganic compound, 25% in the direction of alkali cellulose formation and organometallic alkyl compounds and about 50% of the methoxyls were completely unaffected. Thus partially desoxidated methyl celluloses were obtained. We treated [10] industrial ethyl cellulose (46.8% OC_2H_5, degree of substitution 2.4) with sodium in liquid ammonia.

Partial cleavage of the ethoxyls with the formation of desoxy groups was observed and a corresponding amount of ethyl alcohol was isolated from the reaction mixture. The product obtained was shown to contain a small amount of methyl groups instead of primary alcohol groups by the formation of methylfurfural during decomposition of the product with 12% hydrochloric acid. However, it was impossible to attain a considerable cleavage of ethoxyl groups of ethyl cellulose by the action of sodium in liquid ammonia.

Considering the fact that the action of acrylonitrile on cellulose in the presence of alkali gives cyanoethoxyl ethers of cellulose, while the reverse cleavage of acrylonitrile from cyanoethoxylcellulose is possible in the presence of alkali, one would expect the more ready cleavage of cyanoethoxyl groups. We performed the experiments described below on the desoxidation of this ether of cellulose (I) by the action of sodium in liquid ammonia.

As these experiments showed, cyanoethoxylcellulose was partly desoxidated in this way, but the direct cleavage of acrylonitrile mainly occurred. We isolated desoxycellulose (II), free from ether groups. There was no noticeable formation of carboxyethylcellulose $[C_6H_{10-x}O_{5-x}(OCH_2CH_2COOH)_x]_n$, as is possible if the nitrile groups of the original ether are hydrolyzed [11], but the reaction products did contain acrylic acid (IV) and polyacrylonitrile (V). The acrylic acid may be obtained through β-hydroxypropionic acid (III).


$[C_6H_{10-x}O_{5-x}(OCH_2CH_2CN)_x]_n$
(I)
$CH_2OHCH_2COOH + [C_6H_7O_2H_x(OH)_{3-x}]_n$
$(C_6H_{10}O_5)_n + (-CH_2-CH(CN)-)_n$
(III)
(II)
(V)
$CH_2{=}CHCOOH$
(IV)

That desoxycellulose (II) had actually been obtained in our experiments was confirmed by analysis of the desoxycellulose preparation and the acetates and nitrates prepared from it:

$$[C_6H_7O_2H_x(OR)_{3-x}]_n, \text{ where (VI) } R{=}COCH_3, \ \text{(VII) } R{=}NO_2$$

We did not find propionitrile or propionic acid in the reaction products from sodium treatment of cyanoethoxylcellulose, indicating the absence of the metalloorganic compound of the nitrile (VIII) and propionic acid (IX) from the reaction products.

$$\underset{\text{(VIII)}}{CH_2NaCH_2CN} \rightarrow \underset{\text{(IX)}}{CH_3CH_2COOH}$$

To increase the degree of desoxidation, it is necessary to re-treat the cyanoethoxylcellulose with sodium in liquid ammonia. The reaction first proceeds under homogeneous conditions and then under heterogeneous conditions as cyanoethoxylcellulose dissolves in liquid ammonia and the desoxidated product does not. There is still a great amount of work to be done in studying the properties of desoxycellulose and developing methods for its preparation.

EXPERIMENTAL

The synthesis conditions were chosen and several samples of cyanoethyl ethers of cellulose made and treated with sodium in liquid ammonia to remove the cyanoethoxyl groups by two modes – desoxidation and elimination of acrylonitrile. The desoxycelluloses obtained were characterized as they were and also in the form of the acetates and nitrates.

Synthesis of cyanoethoxylcellulose (I). Syntheses for this cellulose ether are described in the literature; for example: 1) from acetylcellulose in 2% aqueous sodium hydroxide solution with a large excess of acrylonitrile [12] with a degree of substitution of 2.32 (% N 11.4) and 2) by the direct action of excess acrylonitrile on viscose [13].

In this work we used the synthesis for this ether, developed previously in our laboratory (S. N. Danilov, P. T. Pastukhov and A. A. Lopatenok). For the synthesis we used cotton (with a viscosity of 30,56 and 530 cp) or sulfite cellulose, used for the production of viscose (with a viscosity of 30-56 cp). The degree of substitution in the ethers of cotton cellulose was lower (about 2) than in the wood cellulose (about 2.5).

Broken-up cellulose was steeped in 16 volumes of 18% sodium hydroxide solution for 2 hours, pressed out (to three times the weight of the cellulose) and ripened at 18° for two days in a jar, closed with a cork.

The alkali cellulose contained 29.5-30% of α-cellulose and 16% of sodium hydroxide. Since the addition of acrylonitrile to alkali cellulose produces the evolution of heat, promoting hydrolysis of the acrylonitrile and its polymerization, the synthesis was performed by the gradual addition of acrylonitrile over a period of 2 hours with cooling. The mixture was then left at 18° for one or two days. To prevent the formation of a jelly-like mass and darkening, as was observed with 20 moles of acrylonitrile to 1 mole of cellulose, in the experiments described below, 6-12 moles of acrylonitrile was used in the preparation of cyanoethoxylcellulose; the ether retained the fibrous form of the original cellulose under these conditions and the yield was quantitative, calculated on cellulose.

The colorless fibrous samples of cyanoethoxylcellulose contained 8.5-10% nitrogen (degree of substitution 1.5-2) and were neither soluble in cuprammonium solution nor in any organic solvent, though they swelled noticeably in acetone. They were used for the synthesis of desoxycellulose. The preparations did not contain sodium so that it was not necessary to treat them with mineral acid to decompose salts; during combustion with sulfuric acid they did not leave sodium sulfate. This proved that the product did not contain carboxyl groups, which could have been formed by hydrolysis of the nitrile groups.

Synthesis of desoxycelluloses and their properties. For the preparation of desoxycellulose, an apparatus was set up, consisting usually of a wide reaction tube, placed in a Dewar vessel for cooling (with solid carbon dioxide and acetone) and fitted with a gas inlet tube going to the bottom for the admission of ammonia, a funnel (with a stopper) for the introduction of solid reaction components and an outlet tube up through the stopper for the outlet of gases, which were then absorbed in receivers. Gaseous ammonia from a tank was lead through a flowmeter into drying columns (solid sodium hydroxide and soda lime) and the air was flushed from the apparatus with dry ammonia. The dried cellulose ether was first dissolved in liquid ammonia (pale pink solution) and then sodium introduced in small pieces, when a blue solution was obtained. The reaction was performed at the temperature of the cooling mixture and in some cases, at the boiling point of liquid ammonia. The solution was stirred by the passage of the ammonia stream. In some experiments the reaction was performed in a three-necked flask, fitted with a stirrer (stirring for 2-5 hours) for more vigorous stirring. When the components had reacted, the reaction vessel was removed from the cooling mixture and the ammonia removed through a tube with soda lime. Then moist ether was carefully added to decompose the metalloorganic compounds and then methyl alcohol to destroy the unreacted sodium. The alcoholate was then decomposed with water. It was not advantageous to change this order of introducing the reaction components, i.e., to add the fibrous cellulose ether to a solution of sodium in ammonia, as, in this case, acrylonitrile polymer was deposited on the fiber, hindering the reaction.

TABLE

Properties of Original Cellulose Ethers and Desoxycellulose

Name of compound	Found (in %)				Formula of a unit of the compound (calculated)
	C	H	N	CH_3COOH or NO_2 & degree of substitution	
Cyanoethoxylcellulose (I)	—	—	8.81	—	$C_6H_7O_2(OH)_{1.46}(OCH_2CH_2CN)_{1.54}$
Desoxycellulose (II)	46.4	6.45	—	—	$C_6H_7O_2H_{0.45}(OH)_{2.55}$
Acetyldesoxycellulose (IV)	49.29	6.35	—	47.2/2.6	$C_6H_7O_2H_{0.45}(OCOCH_3)_{2.55}$
Nitrodesoxycellulose (VII)	—	—	—	13.2/2.6	$C_6H_7O_2H_{0.45}(ONO_2)_{2.55}$

300 ml of liquid ammonia was condensed onto 10 g of cyanoethoxylcellulose (degree of substitution 1.54) and 5 g of sodium introduced.

In a series of experiments, we established the effect on the course of the cleavage of cyanoethoxyl groups of: 1) the concentration of cellulose ether and sodium in the solution, which are of particular importance, and 2) the reaction time. Under homogeneous reaction conditions, it was necessary to treat the cellulose ether for about 12 hours with 20-24 g-atoms of sodium per glucose residue (about 6 atoms per hydroxyl) and up to 100 ml of liquid ammonia per g of cellulose ether.

If the product still contained nitrogen after the first treatment, a second treatment was necessary and this proceeded under heterogeneous conditions due to the insolubility of desoxycellulose in ammonia. The product was washed and dried after the first treatment and retarded with 6 atoms of sodium per ether group at the boiling point of ammonia for 6 hours. Careful stirring was necessary. The cellulose chains were not disrupted, even after many treatments; the yields of product were good. After removal of the ammonia, it was necessary to add moist ether and then alcohol to the vessel to decompose sodioorganic compounds and to convert the sodium into alcoholate, otherwise, an explosion could occur. The wash liquids were collected to examine the nature of the side products (acrylic acid, etc). The desoxycellulose obtained was acetylated by the usual method with a mixture of acetic anhydride and acetic acid (1 : 1) with a catalyst (perchloric acid) in a ratio of 1 : 14 for 24 hours. The product was insoluble in the acetylation mixture in contrast to normal acetylcellulose. The acetylation product was isolated and prepared for analysis in the usual way. A second acetylation did not change the acetylation product. The acetyl number or else the acetic acid content corresponded to the composition found for the desoxycellulose, which was acetylated. The same desoxycellulose samples were nitrated with nitric acid in methylene chloride. The nitro product also corresponded to the composition of desoxycellulose, in which 0.45 out of the three hydroxyls had been reduced. Comparison of the original ether of the desoxidated cellulose and its acetate and nitrate (see Table) confirmed that partially desoxidated cellulose had actually been obtained from the cyanoethoxycellulose.

The desoxycellulose was analyzed for methyl-group content by hydrolysis with 12% hydrochloric acid; this gave an amount of the phloroglucide of methylfurfural corresponding to 3.4% of methylpentosans or 0.04 desoxy groups for every 3 hydroxyls in the cellulose unit; consequently, there were about 0.4 methylene groups per glucose unit in the desoxycellulose. Available data on the fact that in the synthesis of cellulose ethers the secondary hydroxyls are predominantly etherified, give grounds for thinking that in cyanoethoxylcellulose, the ether groups are mainly at positions 2 and 3 and that they are partially desoxidated, but this requires proof.

Some confirmation of the course of the desoxidation reaction is provided by the fact that the reaction products contained only one product – acrylic acid. We could not detect either propionitrile or propionic acid, which could have been formed had the group been eliminated as the sodioorganic compound (formulas VIII and IX). Ethylene cyanohydrin and hydracrylic acid were not detected, probably due to dehydration of the hydracrylic acid.

When the desoxycellulose had been filtered from the reaction mixture, the residual alkaline aqueous ether-alcohol liquid was acidified and acrylic acid isolated, as proved by rapid bromination and analysis of the lead salt.

Found %: Pb 58.8. Calculated %: Pb for the acrylic acid salt 59.3%. Propionic acid was not found.

SUMMARY

1. When treated with metallic sodium, cyanoethoxylcellulose completely loses the cyanoethoxyl groups, partly in the form of acrylic (hypothetically, hydracrylic) acid, to form methylene groups and partly methyl groups in the glucose units instead of alcohol groups, i.e., to form desoxycellulose.

Part of the cyanoethoxyl groups are eliminated with the formation of desoxy groups and the other part in the form of acrylonitrile due to the reversal of cyanoethylation in an alkaline medium.

2. The presence of desoxy groups in the product was confirmed by analyses of the product obtained and its acetate and nitrate.

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ANHYDRO, DESOXY AND UNSATURATED DERIVATIVES OF POLYSACCHARIDES

II. THE SYNTHESIS OF ANHYDROCELLULOSE FROM p-TOLUENESULFONIC ESTERS

S. N. Danilov and A. A. Lopatenok

Anhydro derivatives of monosaccharides and polyhydric alcohols are known with various sizes and positions of the oxide rings.

In a series of cases, the anhydrides of monosaccharides, especially with 3,6-, 5,6- and 2,3-rings, are synthesized through the p-toluenesulfonic (tosyl) esters and sometimes through halogen derivatives of the monosaccharides by the action of alkaline agents [1].

There is only one paper [2] in which there is a description of the preparation of anhydrocellulose in the form of the mixed tosyl and acetic esters from the mixed tosyl and acetic ester of cellulose by the action of 1 N sodium hydroxide solution in methyl alcohol.

To synthesize anhydrocellulose, whose composition may be represented by the general formula $(C_6H_{10-2x}O_{5-x})_n$, tosyl esters of cellulose $[C_6H_{10-x}O_{5-x}(OSO_2C_6H_4CH_3)_x]_n$ of various degrees of esterification were treated with sodium in liquid ammonia or with organic bases (piperidine,etc) [3].

The use of piperidine for the elimination of p-toluenesulfonic acid gave cellulose derivatives, evidently of an anhydride nature, containing chemically bound piperidine and partly unremoved tosyl groups, which complicated the characteristics of the substances obtained [4].

Below, samples of anhydrocellulose are described, which were prepared by the action of sodium in liquid ammonia on tosylcellulose and whose composition was confirmed by analysis of them and their acetates. It is clear that the removal of tosyl groups may proceed 1) with the formation of anhydro rings or 2) as a result of hydrolysis, which is inevitable in the case of highly tosylated esters.

Since tosyl groups in cellulose are predominantly on primary alcohol groups [5], partially on secondary alcohol groups and very slightly on tertiary alcohol groups, it can be postulated that in our samples of anhydrocellulose, the anhydro rings were between the 6th and 2nd or 3rd atoms of the glucose unit, between the 5th and 6th atoms and, to a lesser extent, between the 2nd and 3rd atoms. In the latter case one would expect transposition [1] of the hydrogen atom and the hydroxyl group at the second and third alcohol groups of the glucose unit of the cellulose molecule (Walden inversion). The problem of the nature and the position of the anhydride rings in anhydrocellulose requires special study.

EXPERIMENTAL

Several samples of fibrous tosyl cellulose (p-toluenesulfonic esters of cellulose) of different degrees of substitution were prepared, experiments performed on the action of sodium in liquid ammonia on them and the composition of the anhydro derivatives of cellulose formed and their acetates determined.

Preparation of tosylcellulose samples. For the syntheses we used normal purified (factory) cotton cellulose (viscosity 56 cp), which was first activated by precipitation from 3% cuprammonium solution or by mercerization in 18% sodium hydroxide, then washed with water and dried with dry pyridine, or heated in pyridine at 70° for 70 hours. The tosyl esters, used for the preparation of anhydrocellulose, were synthesized from cotton cellulose by the action of p-toluenesulfonyl chloride (m.p. 69°) in a pyridine medium. This gave fibrous esters, which

TABLE 1

Sample No.	Number of moles		Time (in hours)	Sulfur found (%)	Composition
	p-toluene-sulfonyl chloride per glucose unit	pyridine per glucose unit			
1	10	120	2	3.76	$C_6H_7O_2(OTs)_{0.25}(OH)_{2.75}$
2	5	20	5	8.06	$C_6H_7O_2(OTs)_{0.67}(OH)_{2.33}$
3	6 + 6	26	21	11.10	$C_6H_7O_2(OTs)_{1.18}(OH)_{1.82}$
4	6 + 6	26	21	12.70	$C_6H_7O_2(OTs)_{1.65}(OH)_{1.35}$

TABLE 2

Sample No.	Composition of anhydrocellulose	Found (in %)		Calculated (in %)		Composition of acetates	Acetic acid (in %)	
		C	H	C	H		found	calculated
1	$C_6H_7O_2(OH)_{2.5}a\text{-}O_{0.25}$	45.5	6.25	48.7	6.06	$C_6H_7O_{2.25}(OCOCH_3)_{2.45}$	56.6	56.7
2	$C_6H_7O_2(OH)_{1.66}a\text{-}O_{0.67}$	48.14	6.26	48.3	5.80	$C_6H_7O_{2.67}(OCOCH_3)_{1.62}$	44.8	44.7
3	$C_6H_7O_2(OH)_{1.2}a\text{-}O_{0.9}$	49.91	6.09	49.4	5.64	$C_6H_7O_{2.9}(OCOCH_3)_{1.15}$	35.5	35.6
4	$C_6H_7O_2(OH)_{0.9}a\text{-}O_{0.9}$	51.2	6.53	51.17	5.61	$C_6H_7O_{3.2}(OCOCH_3)_{0.57}$	20.8	20.8

facilitated the cleavage of p-toluenesulfonic acid groups. In our experiments at 15-20°, the regenerated cellulose (from cuprammonium solutions) gave, over 48 hours, cellulose esters with a sulfur content of 13-14% (degree of substitution 1.8-2.2), which were readily soluble in organic solvents. Cotton cellulose, mercerized in 18% sodium hydroxide for 2 hours, formed tosyl esters over 24-48 hours (with 7 moles of p-toluenesulfonyl chloride per glucose residue) with a degree of substitution of 1-2, but with a yellowish color.

Cellulose activated with pyridine by prolonged heating gave a degree of substitution of from 1 to 1.9 on repeated treatment with p-toluenesulfonyl chloride for from 2 to 21 days at 15-20°. At the end of the reaction, the tosylation mixture was poured into water or aqueous alcohol and the filtered product washed with water, methyl alcohol and ether. The samples obtained were insoluble in organic solvents and swelled in pyridine.

Table 1 gives the preparation conditions and composition of tosyl esters of cellulose (activation of cotton with pyridine), used for the synthesis of cellulose anhydrides.

The sulfur content of the cellulose tosyl esters was determined by oxidation with nitric acid and bromine, with a subsequent alkaline fusion and gravimetric analysis.

Cleavage of p-toluenesulfonic acid from tosylcellulose. A sample of tosylcellulose was placed in a reaction vessel, into which was condensed ammonia. Metallic sodium (6 g-atoms per glucose unit of the cellulose ester) in small pieces, which had been washed in dry ether, was introduced. The reaction lasted for 12-48 hours depending on the degree of esterification of the cellulose. The p-toluenesulfonic acid was cleaved completely from samples 1 and 2 of tosylcellulose in 12 hours; in the case of sample 3, 2 treatments of 12 hours each were required and the p-toluenesulfonic acid was completely cleaved from sample 4 after one treatment for 48 hours with 7.5 g-atoms of sodium per glucose unit of the molecule. From 25 to 75 ml of liquid ammonia was used per gram of tosyl ester.

The anhydro derivatives of cellulose obtained dissolved partially in Schweitzer's cuprammonium solution and in 10% sodium hydroxide, did not contain halogen or sulfur, did not rapidly decolorize a solution of potassium permanganate and contained less than 1% of methylpentosans.

The samples of anhydrocellulose obtained were acetylated with a mixture of acetic anhydride and acetic acid (14 g per g of anhydrocellulose) with a catalyst, perchloric acid, for 24 hours at 20°. The product did not dissolve in the acetylating mixture, which is characteristic of the acetylation of cellulose with this acetylating mixture. The reaction mixture was poured into a 20-fold excess of cooled water to precipitate a colorless or slightly yellowish, fibrous product, which was washed with water, alcohol and ether. Samples were ground and sieved for analysis for acetyl groups. Analyses of the anhydrocelluloses and their acetates indicated that anhydrocelluloses of the given compositions had been obtained in our experiments.

Table 2 gives the compositions of the anhydrocelluloses and their acetates, which may be represented by the general formulas: $[C_6H_7O_{2+x}(OR)_{3-2x}]_n$ or $[C_6H_7O_2(OR)_{3-2x}a\text{-}O_x]_n$, where a-O is the oxygen atom of the anhydro ring, $\underline{x}$ the number of them per glucose unit, and 3-2x the number of residual hydroxyls, while R = H or $COCH_3$.

Despite some comparatively small discrepancies (in Table 2), especially for samples 3 and 4, one can consider that the compositions of the anhydrocelluloses and their acetates agree quite well, within the limits of normal analysis error.

SUMMARY

1. The action of sodium in liquid ammonia on p-toluenesulfonic (tosyl) esters of cellulose gave samples of anhydrocellulose. The composition of the anhydrocelluloses was confirmed by the analyses of the samples themselves and of their acetates, which satisfied the general formulas of the compounds obtained, within the limits of analytical error.

2. When tosyl esters of cellulose, containing more than 1 tosyl group per glucose unit, were treated with sodium in liquid ammonia, p-toluenesulfonic acid was cleaved with the formation of anhydro rings and other tosyl groups were hydrolyzed.

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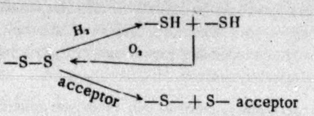
THE CHEMISTRY OF XANTHATES AND VISCOSE

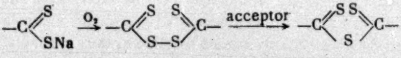
IX. THE DETECTION OF POLYSULFIDE COMPOUNDS IN VISCOSE AND THEIR ROLE

S. N. Danilov, N. F. Gintse and M. G. Okun'

Viscose, alkali cellulose and cuprammonium solutions of cellulose are outstanding among the different products and technical mixtures in complexity and the great peculiarity of the processes in them and the study of the latter is not only of technical, but also of serious theoretical scientific interest. They may be considered to some extent as models of biologically important systems in which an important role is played by oxidation and oxidation-reduction processes and also the phenomena of sulfur transfer and conversions between disulfides and mercaptan groups (conversions of cysteine and cystine and glutathione) [1].



As a result of oxidation by atmospheric oxygen, cellulose xanthate may form dixanthates [2], which are then converted into cellulose thioanhydrides, which were first prepared in our laboratory [3, 4].

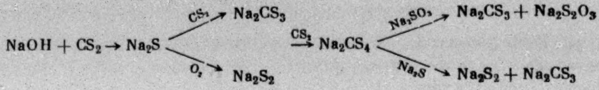


In our papers, data were presented indicating the role of sulfite as an antioxidant [5] and, in particular, as a sulfur acceptor in viscose [6]. Polysulfide compounds (sodium disulfide, perthiocarbonate and thiosulfate) were detected in viscose [7] by means of sodium sulfite and sodium sulfide — sulfur acceptors contained in viscose — by the use of sulfur acceptors foreign to viscose — sodium cyanide and sodium arsenite — and, especially, by the use of tracers [8]. These new facts make it possible to examine the phenomena occurring in viscose during its ripening in more detail.

During the xanthation of alkali cellulose, various sulfur-containing compounds are formed, which are converted by the action of atmospheric oxygen into polysulfide compounds (sodium disulfide, perthiocarbonate and thiosulfate and cellulose dixanthate), capable of donating sulfur to acceptors [7]. Thus, by taking up oxygen, sodium sulfide is an accelerator of the oxidation of viscose components, while sodium sulfite and thiosulfate, like polythionates [6], act as antioxidants. Sodium sulfide, sulfite and possibly thiocarbonate participate in the cleavage of sulfur from polysulfide compounds (from dixanthate and sodium disulfide, perthiocarbonate and thiosulfate).

As viscose ripens, substances accumulate in it in which the ratio of sulfur to sodium increases: from 1 : 2 (Na_2S, Na_2SO_3) to 1 : 1 (Na_2S_2, $Na_2S_2O_3$), then to 3 : 2 (Na_2CS_3) and finally to 2 : 1 (Na_2CS_4), and also the amount of oxygen per sodium atom increases to 1.5-2 atoms ($Na_2S_2O_3$, Na_2SO_3, Na_2SO_4). Sodium sulfite and thiosulfate and finally sodium sulfate are obtained as a result of viscose oxidation.

Apparently, it is precisely the oxidative processes which cause the accumulation of polysulfide compounds in viscose, though they may be partly formed due to free sulfur, if it is present in the technical carbon disulfide. Sodium trithiocarbonate is mainly formed by the reaction of sodium sulfide with carbon disulfide, though, in the presence of oxygen, it may be formed from perthiocarbonate donating its sulfur atom to an acceptor. This is quite possible as sodium disulfide, formed from sodium sulfide by oxidative processes, reacts with carbon disulfide with a geater thermal effect than sodium sulfide [9].



The transfer of sulfur must also be considered in connection with oxidation phenomena in viscose. Other substances of reducing character can also affect viscose similarly to sodium sulfite [10], which is an antioxidant and sulfur acceptor in viscose, but only those, which are capable of adding sulfur, such as cyanides and arsenites [7].

Polysulfide compounds react with sodium hydroxide, which is, to some extent, a sulfur acceptor. Dixanthates and particularly thioanhydrides of cellulose are readily cleaved by alkali [8], and this is accompanied by oxidative cleavage of the dithio group. We previously showed that cleavage of dixanthates with alkali must accelerate the ripening of viscose due to the fact that only half of the cellulose xanthate is regenerated, while the second part of the dithiocarbonate grouping is cleaved [11]. Thus, in the reaction of both sodium disulfide and perthiocarbonate with alkali, one atom of oxygen must be liberated and this will oxidize primarily sulfur products.

It is quite probable that during xanthation and ripening of viscose, some part is played by the oxidizing and reducing groupings in the glucose chains of the cellulose molecules, formed during the preaging of the alkali cellulose, and also products of saccharinic rearrangement and the Cannizzaro reaction (under the action of alkali) of aldehyde groups, produced in alkali cellulose by oxidation. Similar simultaneous oxidation-reduction phenomena were described for the acid conversions of hydroxyaldehydes [12], such as the conversion of hydroxyisobutyraldehyde into isobutyric acid or into the corresponding glycol and hydroxyisobutyric acid. However, these problems have not yet been examined sufficiently for viscose.

Although there is no direct experimental proof as yet, there are grounds for thinking that the ripening of viscose is, in the first instance, the result of hydrolytic and thermal cleavage of dithio groups of xanthate and proceeds by radical- and chain-type reactions. This mechanism is particularly probable for oxidation-reduction processes and sulfur-transfer reactions. We may thus explain the rapidity of the ripening of viscose. The chain of these reactions must begin with oxidative conversion of cellulose xanthate and sodium sulfide (initial products). It continues with sulfur transfer to acceptors and cleavage of polysulfide compounds with the liberation of oxygen. Although polysulfide compounds are inevitably formed in viscose, they are rapidly decomposed in it also. Therefore, analysis indicates a small amount of polysulfide compounds in viscose [8].

Chemical conversions, which are of importance in the ripening of viscose, occur with cellulose xanthate, sodium sulfide, trithiocarbonate, etc.; for example:

1) the number of dithiocarbonate groups in the xanthate gradually decreases due to their hydrolytic cleavage and the liberation of carbon disulfide by the action of heat; the latter is again distributed between xanthate, sodium sulfide and alkali; the trithiocarbonate is partially hydrolyzed to form sodium carbonate and sulfide;

2) as a result of oxidative conversions and the transfer of sulfur atoms to acceptors (sodium sulfite and sulfide and alkali and partially trithiocarbonate), polysulfide and oxygen-containing substances accumulate;

3) cellulose dixanthate and thioanhydride are formed and polysulfide electrolytes transfer their sulfur to acceptors, which affects the distribution of carbon disulfide in the viscose;

4) polysulfide compounds are cleaved by reaction with alkali; this liberates oxygen, which again contributes to the formation of polysulfide compounds, that are also produced by external atmospheric oxygen; it is possible that the reducing groups of cellulose also participate in the conversions;

5) the ripening of viscose, as regards cleavage of dithiocarbonate groups and, in particular, oxidative phenomena and the transference of sulfur, proceeds as a radical and a chain process;

6) as a result of chemical conversions (impoverishment of the xanthate in dithiocarbonate groups and accumulation of electrolytes – soda and sulfur-containing salts) the solubility of the xanthate decreases and the viscosity, structuralization and ripeness of the viscose increase.

We should note that previous ideas on stabilizers and destabilizers of viscose require more accurate definition and we considered this in connection with the problem of the interaction of components in viscose. It is necessary to consider precisely the alkalinity of the medium, the whole complex of viscose components and the nature of the cation and anion of the salts [13]. The rate of decomposition of xanthate in the presence of electrolytes is connected with its precipitation in viscose. This phenomenon was previously considered as coagulation or gelling of the viscose.

As is known, the addition of sodium sulfite to viscose slightly retards the decomposition of xanthate in it and slightly less trithiocarbonate is formed, although the main direction of the reactions during ripening is largely maintained. The ripeness according to the salt index and the ammonium chloride number and also the viscosity of the viscose are slightly reduced by the addition of sulfite. The colloidal-chemical action of sulfite is connected with its salt-electrolyte nature and its chemical action as a sulfur acceptor and an antioxidant, which hinders the formation and accumulation of polysulfide compounds in viscose. As previous experiments in our laboratory showed, due tothis the addition of sulfite to viscose makes it possible to raise the concentration of cellulose in viscose (to 9-9.5%) and slightly lowers the evolution of carbon disulfide during spinning.

In his time, E. Heuser put forward the theory that the reduction in the viscosity of viscose after oxygen has been passed through it, if it is not connected with destruction of the cellulose, may be explained by changes in the "coagulating" action of the mineral components of viscose, due to their oxidation [14]. In the light of the information presented above, in the absence of cellulose destruction, the reduction in the viscosity of viscose may indicate that the oxidation of viscose components proceeds mainly in the direction of sulfite formation.

We should note that the addition of other sulfur acceptors (sodium arsenite and expecially cyanide) to viscose also retards the ripening of viscose, raises the salt index and lowers the viscosity of viscose. However, if sodium sulfite, cyanide and arsenite are added to 2% aqueous solutions of purified xanthate in amounts of 0.3 to 0.5% of the solution weight, then the gelling of solutions is accelerated (experiments of A. F. Vorob'eva). This is additional confirmation of the fact that the action of sulfite on viscose is mainly connected with chemical action with viscose components and not with its role as an electrolyte.

We previously reported the role of the alkalinity of the solution in the action of electrolytes (viscose components) on the ripening of viscose and solutions of purified xanthate [13].

The introduction of polysulfide substances into viscose affects its viscosity and the salt number of its ripeness, but in the opposite way to the introduction of sulfur acceptors. According to experiments (of E. Shimanskaia) in our laboratory, which for brevity we will not describe, the introduction of polysulfide compounds [sodium (perthiocarbonate and disulfide)] into viscose in amounts of 0.3-0.5% of the weight of viscose produces a rapid gelling of the viscose with the effect falling in the series:

$$Na_2CS_4 > Na_2S_2 > Na_2CS_3 = Na_2CS_4 + Na_2SO_3 > Na_2S = Na_2S_2 + Na_2SO_3 > Na_2SO_3 .$$

To detect and determine the amounts of polysulfide compounds in viscose, we tried potentiometric and spectrographic methods and also chromatography. It was found that the donors and acceptors of sulfur in viscose are interconnected and form three pairs of substances, which are determined together by potentiometric titration: 1) Na_2SO_3 and $Na_2S_2O_3$, 2) Na_2S and Na_2S_2, 3) Na_2CS_3 and Na_2CS_4. This hinders their separate quantitative determination. The determination of polysulfide compounds is particularly unreliable in the presence of alkali and soda, probably due to chemical interaction.

The spectra of viscose components, including polysulfide compounds, are quite characteristic, making it possible to determine disulfide and perthiocarbonate in viscose.

1. Determination of Polysulfide Compounds in Viscose

(From the experiments of N. F. Gintse and with the participation of V. V. Vinogradova)

In addition to the usual methods of viscose analysis, based on iodometry in conjunction with methods of precipitating viscose components in the form of cadmium and zinc salts and on determinations of carbon disulfide and hydrogen sulfide with decomposition of the viscose by mineral acid, a method of characterizing viscose by potentiometric titration has been developed recently. In recent years attempts have been made to analyze viscose chromatographically and especially to separate xanthate from low molecular components by mean of ion-exchange

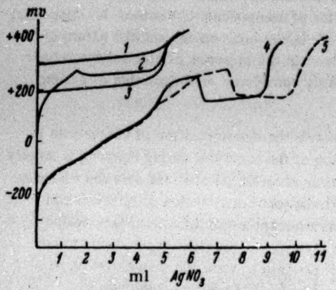


Fig. 1. Potentiometric titration of aqueous solutions of salts and sodium hydroxide with silver nitrate.
1) Sodium carbonate; 2) sodium sulfite; 3) sodium hydroxide; 4) sodium thiosulfate; 5) a mixture of sodium sulfite and thiosulfate.

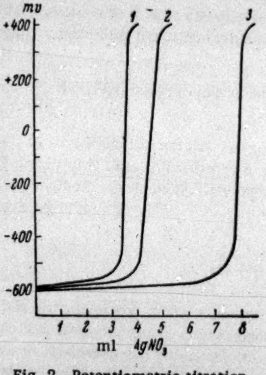


Fig. 2. Potentiometric titration with silver nitrate of aqueous solutions of sodium trithiocarbonate and perthiocarbonate.
1) Trithiocarbonate; 2) perthiocarbonate; 3) mixture of trithiocarbonate and perthiocarbonate.

resins [15]. Methods have been developed in our laboratory for the total determination of polysulfide compounds, based on their donation of a sulfur atom to acceptors, such as sodium cyanide, sulfite and arsenite [6-8]. In looking for methods of determining polysulfide compounds separately, we examined the potentiometric titration of viscose and model solutions of its components by silver nitrate with a silver electrode and also attempted to find conditions for the chromatographic separation of viscose components. The results of these experiments are presented below.

Figure 1 shows titration curves of aqueous solutions of the first pair of viscose components which interested us, namely sodium sulfite and thiosulfate, and also of sodium hydroxide and carbonate, which are titrated in a nearby potential region. We should note that in the titration of aqueous solutions of sulfite we had to add an oxidation inhibitor (0.005 mole/liter of ethylenediaminetetraacetic acid) to suppress oxidation of the sulfite during the titration so as to obtain reproducible results. In the presence of inhibitor, readily reproducible results were obtained, which agreed accurately with the data of iodometric analysis. The presence of an ascending section on the sulfite titration curve in the range from 0 to + 250-280 mv is caused by solution of the silver sulfite formed in excess sodium sulfite to form a binary salt. It is recommended that the determination of thiosulfate by potentiometric titration with silver nitrate using a silver electrode is performed in the presence of sodium acetate at 0° or 80-90° [16] and it is stated that the equilibrium potentials are established slowly due to decomposition of the initially formed binary sodium silver thiosulfate with the formation of silver sulfide. The jump in potential at the end of the titration occurs at a ratio of $Ag^{\cdot} : S_2O_3^{\cdot\cdot} = 1:1$. At normal temperature and in the absence of additions, the titration curve of thiosulfate (Fig. 1) has a completely ascending section in the potential range from − 200 to + 250 mv (formation of binary salt), a small plateau at + 250 mv, a peak with a reverse potential jump and a longer plateau at + 160 − 180 mv (decomposition of binary salt). The titration ends with a $Ag^{\cdot} : S_2O_3^{\cdot\cdot}$ ratio of about 2:1. The first portion of the curve ($Ag^{\cdot} : S_2O_3^{\cdot\cdot}$ ratio = 1:1) is always reproduced well in parallel determinations and the second, with less accuracy. Equilibration of the potentials occurs very slowly throughout the whole titration. The variation in potential in the region of the ascending section of the curve, ending in the peak with the reverse potential jump, is so characteristic that it makes it possible to detect thiosulfate in very small amounts, for example, as very slight traces in preparations of sodium sulfide and disulfide or thiocarbonates. However, the positions of the titration curves of thiosulfate and sulfite and the configurations of these curves are so similar that it is impossible to distinguish sulfite in mixtures with thiosulfate. The combined curve of a mixture of these components differs little from the titration curve of thiosulfate solution (Fig. 1). In the determination of these components in viscose, the problem is further complicated by the proximity of the titration region of sodium hydroxide (+ 220-240 mv) and soda (+ 300 mv). The old method of determining thiosulfate and sulfite by Kurtenaker's procedure cannot be replaced by the potentiometric method.

Figures 2 and 3 show the silver nitrate titration curves of aqueous solutions of sodium sulfide and disulfide and tri- and perthiocarbonates. Each of these components is titrated accurately and clearly alone and gives a sharp potential jump at the equivalence point with good agreement between the potentiometric and iodometric determinations. We previously reported [13] that the potentiometric determination of trithiocarbonate was possible only as the total with perthiocarbonate and sulfide, with disulfide. The titration curves of aqueous solutions of trithiocarbonate and perthiocarbonate are completely identical, as can be seen, and merge into one continuous curve in the titration of a mixture of these salts (Fig. 2). The total content of these salts of an aqueous solution was determined quite accurately.

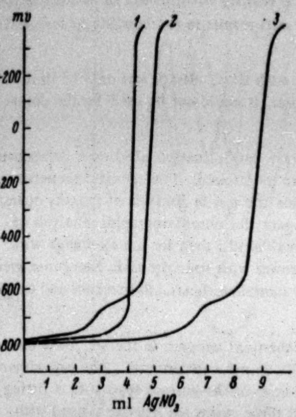


Fig. 3. Potentiometric titration with silver nitrate of aqueous solutions of sodium sulfide and disulfide.
1) Sulfide; 2) disulfide; 3) mixture of sulfide and disulfide.

The titration curve of sodium disulfide differs from that of sodium sulfide in the presence of an additional plateau at + 650 mv (Fig. 3). The first plateau corresponds to the precipitation of silver sulfide ($NaS_2S + 2Ag \rightarrow Ag_2S + S$) and the second (in the opinion of Sack [17]) is caused by the discharge of colloidal particles of Ag_2S-S. When alkali is added to the disulfide solution, this plateau dissappears. In the titration of a mixture of aqueous solutions of disulfide and sulfide, there is a quantitative merging of the main plateaus of the individual curves, but the character of the additional disulfide plateau is retained (Fig. 3). Thus, while it is impossible to separate sulfide and disulfide quantitatively in mixtures, it is possible to detect disulfide in them qualitatively. The disappearance of the second plateau on the titration curve of disulfide on the addition of alkali, makes it impossible to detect disulfide even qualitatively in alkaline solutions and consequently in viscose from potentiometric-titration curves. We should note that the presence of sulfide or disulfide in mixtures of tri- and perthiocarbonate does not interfere with the determination of the latter by potentiometric titration with silver nitrate and likewise, the presence of tri- or perthiocarbonates in the solution does not interfere with the determination of mono- and disulfide.

In the potentiometric titration of alkaline solutions of disulfide [13], trithiocarbonate and perthiocarbonate with silver nitrate, high results are obtained as a certain amount of alkali (up to 2 moles per mole of salt) is titrated together with the salt. This phenomenon was reported for solutions of trithiocarbonates by Herrent and Inoff [18] and Zav'ialova [19], but in a slightly different qualitative ratio by the latter. We titrated mixtures of trithiocarbonate, disulfide and perthiocarbonate with sodium hydroxide, prepared immediately before titration, over a wide range of potentials, which made it possible for us to observe the changes in the precipitation plateaus of sodium hydroxide. The latter were noticeably decreased in the presence of each of the given salts and with a sodium hydroxide content of less than 2 moles per mole of salt in the mixture, they disappeared completely. The precipitation plateaus of the salts increased correspondingly and reached a maximum at slightly less than double the original value, with a sodium hydroxide content in the mixture of 2 moles per mole of salt. With a further increase in the alkali content, the values of the plateaus of disulfide hardly changed and the plateaus of the thiocarbonates contracted slightly. These phenomena are connected with the partial decomposition of the salts during the titration as is indicated by the course of titration curves of mixtures. A new region of difficultly establishable potentials in the range from − 300 to + 200 mv appears on all the curves and, in the presence of trithiocarbonate or perthiocarbonate, a new plateau appears in the region of sodium carbonate precipitation. With an increase in the alkali content of the mixture, the decomposition of the salts increases. The results of our experiments on the titration of alkaline solutions of disulfide, perthiocarbonate and trithiocarbonate, which show that 2 moles of sodium hydroxide are titrated with 1 mole of each of the salts, agree with the data of Herrent and Inoff [18] on trithiocarbonate.

The instability of disulfide and perthiocarbonate, observed in alkaline solution, results in a low content of polysulfide compounds in the viscose (the fact that cellulose dixanthate is readily decomposed in alkali was reported previously [2, 11]). As we saw, the decomposition of polysulfide salts results in the bonding of free sodium hydroxide.

Experiments showed that direct potentiometric titration of viscose with silver nitrate was only of limited application for characterizing the composition of viscose and, in particular, it could not be used for the determination of its polysulfide components.

The problems in the use of chromatographic methods for the separate determination of viscose components were not considered in the works of Samuelson and Geiger [15], that were mentioned. The specific properties of viscose components, their diversity, and most of all, low stability, exclude the use in analysis of lengthy operations and high dilutions and raise considerable difficulties in the choice of reagents for chromatographic analysis of viscose. Since the components of viscose are salts of strong bases and weak acids, then for ion exchange with them under alkaline conditions, it is only possible to use ion-exchange resins with strongly basic ionogenic groups, for example, with quaternary ammonium-base groups, which are clearly monofunctional. Samuelson and Geiger used Amberlite IRA-400 and Dowex-1.

The strongest anionite of our resins is PEK, but it only has low mechanical strength in the wet state and therefore we also used two slightly less strong anionites, PE-9 and EDE-10, in our experiments. The experiments were performed with the hydroxyl form of the resin in ion-exchange columns of the normal type with a fitting ensuring filtration at constant pressure. The experiments showed that all three resins readily exchanged with trithiocarbonate and perthiocarbonate and more difficultly with sulfides, especially the resin EDE-10. For each of the resins investigated, working conditions were found so that the side products were removed quantitatively from the viscose and completely pure xanthate was obtained as filtrates containing only sodium hydroxide in addition to the xanthate. The least advantageous were the conditions for the resin EDE-10, due to its low capacity for exchange with sulfide. The use of the resins PEK and PE-9 gave similar results. The separation of the viscose components absorbed on the anionite layer presented considerable difficulty, largely due to the necessity for diluting the viscose considerably for filtering it through the anionite. Special experiments proved that there was no change in the total distribution of sulfur between the xanthate and the side products during operation on the ion-exchange columns. In this respect, the use of activated charcoal was more favorable as it made it possible to work with less dilute viscoses and at higher filtration rates. Filtration of viscose through activated charcoal quantitatively removed all the side products except thiosulfate; in contrast to ion-exchange resins, charcoal held sulfides more readily than thiocarbonates. Attempts to separate the absorbed components by elution in stages using different salt solutions and certain solvents, did not give positive results, however, in this case.

Further investigations are required on the sorption and chromatographic methods of elucidating the composition of viscose.

2. Spectroscopic Investigations of Viscose

(From the experiments of M. G. Okun')

The investigations of viscose and trithiocarbonate, carried out by Rassow and Aehnelt in the ultraviolet region, are well known [20].

Our spectrographic investigations over a wide range of wavelengths were aimed at examining the spectra of polysulfide compounds (sodium disulfide and perthiocarbonate), as a method of detecting them in viscose. An investigation was made of the absorption spectra of aqueous and alcoholic solutions of sodium disulfide, perthiocarbonate and trithiocarbonate and mixtures of these sulfur-containing substances and also water-diluted industrial viscose and similar solutions to which polysulfide compounds had been added preliminarily.

The experiments were performed on an SF-11 spectrophotometer and the optical density was determined in the visible and ultraviolet parts of the spectrum, using hermetically sealed cells with quartz windows. In all the experiments, the layer thickness equalled 5 mm. An incandescent tungsten filament lamp was used as a light source for the visible region and a hydrogen lamp for the ultraviolet region. The short-wave part of the spectrum was registered on an antimony-cesium photocell and the long-wave part on an oxygen-cesium photocell. The absorption spectrum of a substance was determined by measuring the relative value of the light beam, passing through the absorbing substance, relative to the wavelength.

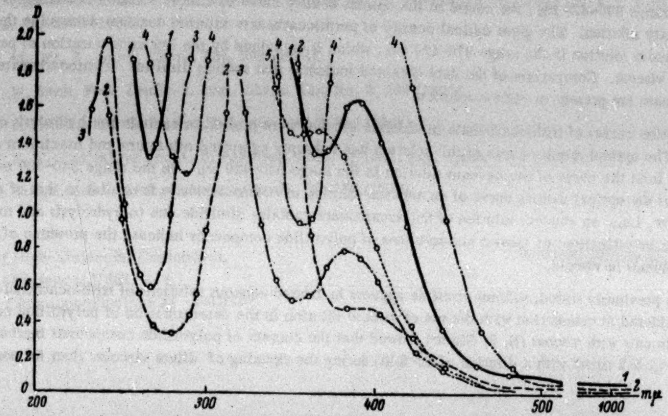


Fig. 4. Dependence of optical density of solutions on wavelength. 1) Aqueous solution of viscose; 2) aqueous solution of sodium trithiocarbonate; 3) alcohol solution of sodium trithiocarbonate; 4) aqueous solution of sodium perthiocarbonate; 5) aqueous solution of sodium disulfide.

An investigation was made of viscose solutions diluted 50, 100 and 200 times and also of trithiocarbonate, disulfide and perthiocarbonate in the form of 0.05, 0.005 and 0.001 molar solutions. The clearest picture was given by viscose solutions diluted 200 times and for separate components, 0.001 molar solutions were convenient.

For the work, sodium perthiocarbonate, trithiocarbonate and disulfide were synthesized in an atmosphere of nitrogen recording to published descriptions [9]. The optical density was determined. Curves were constructed for the dependence of the optical density (D) on the wavelength (λ) (in mμ). Measurements were performed at intervals of 5-10 mμ. Blank readings were performed on the absorption of air in the measurement of the optical density of a solution or on a viscose solution of the same dilution for measurement of the absorption curves of substances dissolved in viscose.

Figure 4 shows the absorption curves for 0.001 molar solutions of polysulfide compounds, transmitting light over a wide wavelength range. An aqueous solution of trithiocarbonate has an absorption minimum at 280 mμ. In the range from 310-350 mμ, the optical density is very great; at 370 mμ the optical density falls sharply; in the range from 370-400 mμ, it is almost constant and then becomes very small (asymptotically approaching the abscissa). An aqueous solution of perthiocarbonate has two absorption minima, one at 290 mμ and the other at 360 mμ; in the ranges 300-340 mμ and 380-410 mμ, the optical density is very large; at 410 mμ the density decreases considerably and then the optical density curve of the solution approaches the abscissa asymptotically. In the range 350-370 mμ, an aqueous solution of sodium disulfide has an almost constant optical density, which then decreases sharply and then remains constant. The diluted viscose solution has an absorption minimum at 270 mμ, the optical density of the solution is very great in the range 280-350 mμ, in the range 350-400 mμ, at 370 mμ–there is a minimum and at 390 mμ a maximum in the optical density and then the optical density of the solution is small.

A comparison of the absorption curves of polysulfide compounds and viscose shows that there is a great similarity in the course of the curves. In the range 240-300 mμ, the optical density of trithiocarbonate is very small, while that of perthiocarbonate solution is considerable. As Fig. 4 shows, the optical density of viscose solution is almost equal to that of perthiocarbonate solution. In the range 300-320 mμ, the optical density of polysulfide compound solutions is very great and viscose solution does not transmit light in this region. In the range 320-370 mμ, the optical density of trithiocarbonate solution is very small. The optical density of viscose is considerably greater in this region. This is explained by the presence of disulfide compounds in the solution. As Fig. 4 shows, in this region the optical density of sodium disulfide solution determines the optical density of viscose solution.

In the range 370-420 mμ, the course of the optical density curve of viscose solution is analogous to that of trithiocarbonate solution. The great optical density of perthiocarbonate solution does not determine the optical density of viscose solution in the range 370-420 mμ, which is explained by the low concentration of perthiocarbonate in viscose. Comparison of the data obtained indicates that sodium disulfide, trithiocarbonate and perthiocarbonate are present in viscose solution.

Absorption curves of trithiocarbonate in absolute alcohol were plotted to exclude the hydrolysis of trithiocarbonate. The optical density curve of this solution has a sharply expressed minimum and maximum and differs considerably from the curve of the aqueous solution in the range 340-420 mμ. In the range 340-420 mμ, the appearance of the optical density curve of an aqueous solution of trithiocarbonate is similar to that of a sodium disulfide curve, i.e., an aqueous solution of trithiocarbonate contains disulfide due to hydrolysis and oxidation. Spectroscopic investigations of viscose and solutions of polysulfide compounds indicate the presence of polysulfide compounds in viscose.

As was previously stated, sodium disulfide appears in diluted aqueous solutions of trithiocarbonate and this must be considered in connection with the use of viscose dilution in the determination of polysulfide compounds in it. Experiments with viscose (N. F. Gintse) showed that the content of polysulfide compounds increased more considerably (1.5-2 times with a dilution of 12-fold) during the ripening of dilute viscoses than for normal viscoses.

SUMMARY

1. There are oxidation-reduction conversions and sulfur-transfer phenomena in viscose, especially in the presence of atmospheric oxygen, which give grounds for considering the ripening of viscose as a model for biologically important systems.

2. While the total content of polysulfide compounds in viscose can be determined with sodium cyanide and sulfite, their separate determination by the potentiometric method presents great difficulties, especially in the presence of alkali. Xanthate may be freed from side products by the use of active charcoal and anionites.

3. The courses of the optical density curves of viscose and trithiocarbonate solutions are analogous; in aqueous solutions of trithiocarbonate, sodium disulfide appears, due to hydrolysis and oxidation.

4. Trithiocarbonate is present in viscose solution in large amounts and perthiocarbonate in small amounts.

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THE FORMATION OF PEROXIDES IN THE OXIDATION OF CELLULOSE ETHERS AND ESTERS*

O. P. Koz'mina, V. I. Kurliankina, E. N. Matveeva and M. K. Aleksandrovich

As was reported in the paper of Danilov and Koz'mina [1] and in subsequent papers [2, 3 and 4], the destruction of cellulose ethers and esters at moderately elevated temperatures and by ultraviolet radiation is caused by their reaction with atmospheric oxygen, which leads to oxidation, cleavage of the oxidized ether or ester group and destruction of the chain. The oxidized ether and ester samples gave a positive reaction for peroxides and it can be postulated that the decomposition proceeds through the intermediate formation of peroxides.

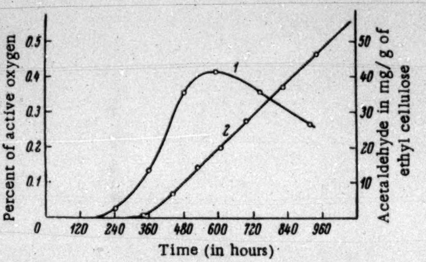

Fig. 1. Oxidation of ethyl cellulose at 70°.
1) Rate of peroxide formation; 2) rate of aldehyde formation.

In the course of further investigations, conditions for peroxide accumulation in cellulose ethers and esters were found and also the character of their formation rate curves, which had a definite maximum (Fig. 1, curve 1). In the same figure, curve 2 shows the rate of acetaldehyde formation in the same experiment. The curves indicate that peroxides were formed first. This is also indicated by direct experiment on the decomposition of peroxide groups in samples of oxidized ethers and esters in an atmosphere of nitrogen.

Peroxides of ethers and esters, especially of esters, are readily obtained by ultraviolet irradiation (Fig. 2). Our experiments show that peroxides of cellulose ethers and esters are comparatively and can be stored for a long period, both as the solid and in solution, which makes it possible to free them from traces of low-molecular substances by dialysis.

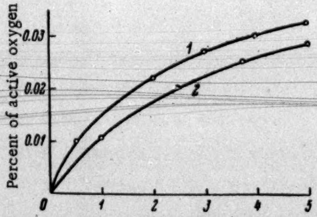

Fig. 2. Rate of peroxide formation in cellulose ethers and esters in ultraviolet light.
1) In acetobutyrate; 2) in ethyl cellulose.

Peroxides of ethers and esters, and also their decomposition products – volatile peroxides and aldehydes – gradually accumulate during storage of the ethers and esters and reduce the induction periods of the thermo-oxidative decomposition of the ethers and esters. If the peroxide groups are destroyed with hydrogen iodide or hyposulfite and the low-molecular impurities washed out by dialysis [2] or the solutions of aged ethers or esters are treated with small amounts of salts of metals of variable valence ($KMnO_4$, or acetates of iron and copper), which are subsequently removed, then induction periods again appear, as are characteristic of freshly prepared samples (Fig. 3).

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* Report V in the series "Investigations in the field of oxidation processes of cellulose ethers and esters with molecular oxygen."

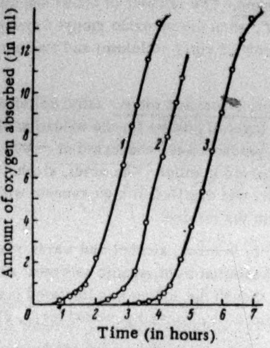

Fig. 3. Effect of preliminary treatment of solutions of aged samples of ethyl cellulose with solutions of variable-valence metal salts on the length of the induction period during oxidation at 130°.
1) Oxidation rate of original sample; 2) oxidation rate of sample treated with copper acetate; 3) oxidation rate of sample treated with iron acetate.

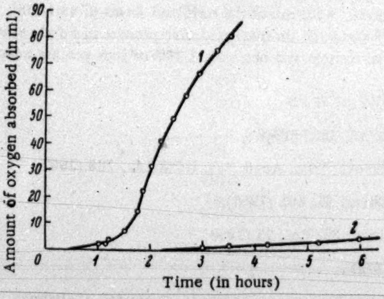

Fig. 4. Inhibiting effect of ferric salts in the oxidation of ethyl cellulose at 130°.
1) Oxidation rate of original sample; 2) oxidation rate of ethyl cellulose sample containing 1.8% of iron acetate.

The reaction with the peroxides, apparently, also explains the inhibiting effect of salts of variable-valence metals and sol impurities (iron) in technical samples of cellulose ethers and esters (Fig. 4).

On the basis of peroxidated ethers and esters of cellulose, the authors and V. I. Gribkova prepared graft polymers with styrene, methyl methacrylate and other monomers with from 2 to 10% of the grafted polymer chains, depending on the amount of peroxide groups in the original ether and ester samples. The formation of graft polymers is a further indication of the presence of peroxides in cellulose ethers and esters.

New data were obtained on the liberation (into the volatile phase [3]) of large amounts of peroxides (up to 30%) during oxidation of the esters and ethers under mild conditions, which probably also throws light on the character of the peroxides of the esters and ethers themselves.

The peroxides formed may serve as a source of formic acid, alcohols and hydrocarbons, as secondary products of the thermo-oxidative decomposition of ethers and esters.

EXPERIMENTAL

For the investigation we used industrial samples of ethyl cellulose with an ethoxyl content of 47.5-48.5%, which were first freed from sol impurities (up to 0.008-0.02%) by precipitation from acetic acid solution with dilute (10%) acetic acid. The cellulose esters were prepared from cotton cellulose of satisfactory purity and then purified in some cases only for comparison. The cellulose acetobutyrate contained 38-45% of butyric and 18-28% of acetic acids.

Preparation of peroxides of cellulose ethers and esters. For preparation of the peroxides, the ethers and esters in thin layers or films were heated or irradiated in a thermostated silica cell in a stream of oxygen, by the method described previously [3]. The most convenient temperature for the dark reaction was 70-90° and at this temperature the greatest amount of peroxides accumulated and it was possible to follow the different rates of their formation and decomposition (Fig. 1); the latter became the same with an increase in temperature. The source of ultraviolet light was PRK-4 lamps placed on both sides along the faces of the cell at a distance of 20 cm. Figure 2 shows the rate of formation of peroxides of esters and ethers during irradiation at 25°. The peroxide groups were determined iodometrically after preliminary dialysis or evacuation of the samples in high vacuum to remove adsorbed low-molecular impurities.

Decomposition of peroxides of cellulose ethers and esters in nitrogen. The samples of ethers and esters, containing peroxide groups, were heated in a stream of nitrogen at 130°, when the peroxide groups decomposed, the characteristic viscosity fell (for example, from 2.0 to 1.8 for a sample of ethyl cellulose) and traces of aldehydes were detected colorimetrically.

Low-Molecular (volatile) peroxides from the oxidation of cellulose ethers and esters. Ethyl cellulose was oxidized in a stream of oxygen at 110° in the form of films and a thin layer of powder (in the oxidation of a thick layer, the peroxide yield fell sharply) and the low-molecular, volatile products were condensed at − 80°. To separate the peroxides, the condensate of the volatile products was dissolved in ether. The acids, alcohol and water were removed with $CaCO_3$, $CaCl_2$ and Na_2SO_4. The ether solution was distilled in high vacuum without heating, then the ether was evaporated and the peroxide concentrated in the residue.

The volatile peroxide had a specific, sharp smell, dissolved readily in ether, alcohol and water, reacted vigorously with lead tetraacetate and was rapidly extracted with alkali solution from organic solvents. At the same time, it reacted sluggishly with potassium iodide in acetic acid, though the iodine was liberated completely on long standing or heating. All these features are characteristic of hydroxyalkyl peroxides [5, 6].

The hydroxyalkyl character was confirmed by the immediate decomposition of the peroxide by mineral acids with the liberation of acetaldehyde [7]. In contrast to dihydroxyethyl peroxide, the peroxide obtained gave 1 mole of acetaldehyde on decomposition; thus, for example, when decomposed with hydrochloric acid, an aqueous solution containing 0.06615 mmole/ml of peroxide gave 0.06586 mmole/ml of acetaldehyde. Acetaldehyde was also liberated on treatment of the peroxide with SO_2. Volatile peroxides were also obtained in the oxidation of cellulose esters.

Effect of variable-valence salts on the oxidation of ethyl cellulose. To acetic acid solutions of aged ethyl cellulose, with reduced induction periods, were added copper and iron acetates (ferric form) and also $KMnO_4$. The acetates were prepared by dissolving the hydroxides in glacial acetic acid and the solutions added to ethyl cellulose in acetic acid. The solutions were kept for a day (with $KMnO_4$, for a longer time – until it was reduced) and then the ethyl cellulose was precipitated with 10% acetic acid. Samples containing traces of iron (0.0115%) and not containing copper and manganese, had longer induction periods in comparison with the originals (Fig. 3), when oxidized as powders and films, prepared on glass. Addition of the oxidized forms of variable valence salts (also as acetates) in amounts of from 0.5 to 2% slows the thermo-oxidative process of ethyl cellulose. Figure 4 shows curves of the oxygen absorption of the original sample and one with 1.18% of iron acetate added.

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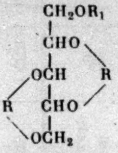
ALLYL AND METHALLYL ETHERS OF ACETALS AND KETALS OF XYLITOL AND XYLITAN*

A. N. Anikeeva and G. M. Zarubinskii

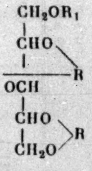
The allyl and methallyl ethers of a series of polyhydric alcohols and carbohydrates have been described, including those of α-methylglucoside [1] and galactoside [2], mannitol, sucrose [3] and others.

We synthesized the allyl and methallyl ethers of acetals and ketals of xylitol and xylitan by treating them with allyl bromide or methallyl chloride in a solvent in the presence of powdered sodium hydroxide. The starting materials – 2,4-3,5-dimethylenexylitol [4], 2,3-4,5-diacetonexylitol [5] and 2,3-4,5-di-benzylidenexylitol [6] were prepared by the methods described in the literature.

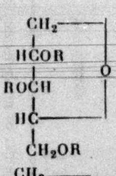
All the xylitol derivatives given above have been shown to contain a free primary hydroxyl group; hence, there is no doubt that the position of the allyl and methallyl groups of the molecules of the derivatives obtained is at the first carbon atom. (Compounds III, IV, V, VI, XII, XIII, XIV and XV).



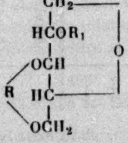
(I) $R = \text{cyclo-}C_6H_{10}$, $R_1 = H$;
(II) $R = \text{cyclo-}C_6H_{10}$, $R_1 = C(C_6H_5)_3$,
(III) $R = CH_2$, $R_1 = CH_2{-}CH{=}CH_2$;
(XIV) $R = CH_2$, $R_1 = CH_2{-}\underset{CH_3}{\underset{|}{C}}{=}CH_2$.



(IV) $R = C(CH_3)_2$, $R_1 = CH_2{-}CH{=}CH_2$
(V) $R = CHC_6H_5$, $R_1 = CH_2{-}CH{=}CH_2$
(VI) $R = \text{cyclo-}C_6H_{10}$, $R_1 = CH_2{-}CH{=}CH_2$
(XIII) $R = C(CH_3)_2$, $R_1 = CH_2{-}\underset{CH_3}{\underset{|}{C}}{=}CH_2$
(XII) $R = CHC_6H_5$, $R_1 = CH_2{-}\underset{CH_3}{\underset{|}{C}}{=}CH_2$
(XV) $R = \text{cyclo-}C_6H_{10}$, $R_1 = CH_2{-}\underset{CH_3}{\underset{|}{C}}{=}CH_2$



(VII) $R = CH_2{-}CH{=}CH_2$



(VIII) $R = CH_2$, $R_1 = CH_2{-}CH{=}CH_2$
(IX) $R = CHC_6H_5$, $R_1 = CH_2{-}CH{=}CH_2$
(X) $R = C(CH_3)_2$, $R_1 = CH_2{-}CH{=}CH_2$
(XI) $R = \text{cyclo-}C_6H_{10}$, $R_1 = CH_2{-}CH{=}CH_2$

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*This article is the 6th report in the series "Anhydrides, and amino- and guanido-derivatives of carbohydrates and polyhydric alcohols;" for the 5th report see J. Gen. Chem. 27, 2434 (1957).

TABLE 1

Allyl Ethers of Acetals and Ketals of Xylitol

Exp. No.	Compound	Boiling point (pressure in mm) or melting point	n_D^{20}	d_4^{20}	MR_D		Yield (in %)	Analysis data (in %)			
								carbon		hydrogen	
					found	calculated		found	calculated	found	calculated
1	1-Allyl-2,4-3,5-dimethylenexylitol $C_{10}H_{18}O_5$ (III)	146°	—	—	—	—	54	55.52, 55.34	55.54	7.61, 7.71	7.46
2	1-Allyl -2,3-4,5-diacetonexylitol $C_{14}H_{24}O_5$ (IV)	106 (0.5)	1.4496	1.0419	70.18	70.20	33	61.86, 61.61	61.70	9.10, 9.09	8.88
3	1-Allyl -2,3-4,5-dibenzylidenexylitol $C_{22}H_{24}O_5$ (V)	157	—	—	—	—	80	71.70, 71.86	71.71	7.21, 7.02	6.58
4	1-Allyl -2,3-4,5-dicylcohexylidenexylitol $C_{20}H_{32}O_5$ (VI)	152 (0.6)	1.4902	—	—	—	87	68.17, 68.20	68.15	8.73, 8.82	9.40
5	2,3,5-Triallylxylitan $C_{14}H_{22}O_4$ (VII)	105—106 (0.8)	1.4692	1.0090	69.93	69.70	75	66.00	66.14	8.80	8.68

TABLE 2

Allyl Ethers of Acetals and Ketals of Xylitan

Exp. No.	Compound	Boiling point (pressure in mm) or melting point	n_D^{20}	d_4^{20}	MR_D		Yield (in %)	Analysis data (in %)			
								carbon		hydrogen	
					found	calculated		found	calculated	found	calculated
1	Allyl ether of methylenexylitan $C_9H_{14}O_4$ (VIII)	88° (1)	1.4750	1.1648	44.59	43.36	48	53.24, 52.90	52.88	7.44, 7.58	7.52
2	Allyl ether of benzylidenexylitan $C_{15}H_{18}O_4$ (IX)	157—158 (0.8)	1.5274	1.1495	69.98	70.03	40	68.93, 68.85	68.74	7.39, 7.19	6.87
3	Allyl ether of acetonexylitan $C_{11}H_{18}O_4$ (X)	135 (1)	1.4652	1.0887	54.36	54.59	84	61.26, 61.46	61.63	8.67, 8.60	8.41
4	Allyl ether of cyclohexylidenexylitan $C_{14}H_{22}O_4$ (XI)	105—106 (0.8)	1.4886	1.1054	66.25	66.28	76	65.93, 66.10	66.14	8.97. 8.82	8.68

TABLE 3

Methallyl Ethers of Acetals and Ketals of Xylitol

Exp. No.	Compound	Boiling point (pressure in mm) or melting point	n_D^{20}	d_4^{20}	Yield (in %)	Analysis data (in %)			
						carbon		hydrogen	
						found	calculated	found	calculated
1	Methallyl ether of dibenzylidenexylitol (XII) $C_{23}H_{26}O_5$	148—149°	—	—	50	72.01, 72.19	72.26	6.98, 6.94	6.80
2	Methallyl ether of diacetonexylitol (XIII) $C_{15}H_{26}O_5$	154—157 (0.8)	1.4534	1.0322	20	62.35, 62.39	62.91	9.27, 9.03	9.15
3	Methallyl ether of dimethylenexylitol (XIV) $C_{11}H_{18}O_5$	133—135	—	—	18	52.87, 57.68	57.41	7.74, 7.96	7.82
4	Methallyl ether of dicyclohexylidenexylitol (XV) $C_{21}H_{34}O_5$	144—147 (0.5)	1.4905	1.0996	56	68.90, 68.92	68.82	9.89, 9.74	9.35

Dicyclohexylidenexylitol, which we were the first to obtain, was synthesized under the conditions used in our experiments on the preparation of cyclohexylidenexylitan [7] (the reaction time was increased from 10 to 30 hours).

To solve the problem of whether there was a free primary hydroxyl group in dicyclohexylidenexylitol, its triphenylmethyl ether was prepared. This shows that the allyl and methallyl groups attached to dicyclohexylidene were at the first carbon atom (VI and XV).

In a previous report [7], we presented data showing that in acetals and ketals of xylitan, the primary hydroxyl group was involved in the formation of the ketal and, apparently, the acetal link, since it was not possible to prepare the trityl ether of any of the compounds. This was confirmed by experiments presented in the previous report, showing that the compounds remaining after hydrolyzing the ketal groups from ketal benzoates could not be oxidized with lead tetraacetate. Consequently, the allyl groups in acetals and ketals of xylitan must be at the second or the third carbon atom (VIII, IX, X, XI).

EXPERIMENTAL

To synthesize dicyclohexylidenexylitol, a mixture of 35 g of xylitol (m.p. 96°), 90 g of freshly distilled cyclohexanone, 200 ml of absolute ether and 5 ml of concentrated sulfuric acid were shaken for 30 hours. The acid was neutralized with soda, the solution evaporated and the residue vacuum-distilled twice. We obtained 38 g (53%) of dicyclohexylidenexylitol as a viscous sirup (I).

B.p. 193° (0.5 mm), n_D^{20} 1.4985.
Found %: C 65.43, 65.48; H 9.46, 9.38. $C_{17}H_{28}O_5$. Calculated %: C 65.40; H 8.90.

The triphenylmethyl ether of dicyclohexylidenexylitol was prepared by reacting 2.9 g of dicyclohexylidenexylitol, dissolved in 20 ml of dry pyridine, and 2.9 g of triphenylmethyl chloride for 48 hours. The reaction mixture was poured into ice water and the viscous mass produced was dissolved in chloroform, washed with water and dried with baked sodium sulfate. The solution was evaporated in vacuum and the residue crystallized completely after 14 days. After two recrystallizations from ethyl alcohol, the triphenylmethyl ether (in the form of fine needles) had m.p. 108° (II).

Found %: C 77.50; 77.48; H 8.05, 7.87. $C_{36}H_{42}O_5$. Calculated %: C 77.94; H 7.57.

Synthesis of allyl and methallyl ethers. The allyl and methallyl ethers were synthesized under identical conditions. The starting material, solvent and powdered alkali were placed in a three-necked flask on an oil bath and fitted with a stirrer, a reflux condenser and a dropping funnel. The allyl bromide or methallyl chloride was added dropwise with vigorous stirring, while the bath was heated to 50-70°. When the halide had been added, the mixture was boiled for 8-10 hours. Then the flask was cooled, the reaction mixture diluted with water and the benzene layer washed, dried with sodium sulfate and evaporated. The residue was either vacuum distilled or recrystallized from alcohol. In most experiments, the allyl ethers were synthesized using the reaction components, ketal or acetal of xylitol, halide and alkali, in the ratio 1:3:4.

The ethers obtained were insoluble in water but soluble in the normal solvents. The properties of the allyl ethers of acetals and ketals of xylitol obtained are presented in Table 1.

For the synthesis of 1,4-anhydro-2,3,5-triallylxylitol, a mixture of xylitan (5 g) was stirred vigorously with allyl bromide (26 g), heated to 70°, then 40% aqueous alkali added from a dropping funnel over a period of 45 minutes and heating continued for 5 hours. The following day, the oily layer was separated from the water, washed free from alkali and dried with sodium sulfate. Two distillations in vacuum yielded 6.9 g (75%) of substance as a thick, colorless sirup.

The analysis corresponded to the formula of the triallyl ether of xylitan (VII).

B.p. 105-106° (0.8 mm), n_D^{20} 1.4692, d_4^{20} 1.0090, MR_D 69.93; calc. 69.70.
Found %: C 66.00, H 8.80. $C_{14}H_{22}O_4$. Calculated %: C 66.14; H 8.68.

Allyl ethers of acetals and ketals of xylitan. The starting materials – methylenexylitan, benzylidenexylitan, acetonexylitan and cyclohexylidenexylitan – were prepared as we described previously [7]. Their allyl ethers were prepared as described above. The characteristics of the allyl ethers of xylitan derivatives are given in Table 2.

Methallyl chloride was prepared by a method described in the literature [8], but with some simplification of the apparatus. The mixture of products obtained (isopropyl chloride, methallyl chloride and dichloroisobutane) was distilled twice on a column. The methallyl chloride obtained boiled at 72° and had the physical properties reported in the literature. The characteristics of xylitol derivatives are presented in Table 3.

The authors would like to thank Prof. S. N. Danilov for directing the work.

SUMMARY

We synthesized allyl and methallyl ethers of acetals and ketals of xylitol and xylitan, which are not described in the literature and are of interest as reactive, unsaturated derivatives of polyhydric alcohols and their anhydrides.

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AMINO DERIVATIVES OF 1,4-ANHYDROXYLITOL*

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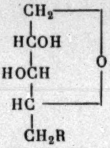
As a development of our previous communication [1], we prepared amino derivatives of xylitan from its chlorohydrin (5-chloro-1,4-anhydroxylitol).

No amino derivatives of xylitol or xylitan are described in the literature. There is also little information on the amination of other polyhydric alcohols. 1,6-Diaminomannitol was prepared from dichlorodimethylene mannitol by heating the latter in an autoclave with ammonia in methyl alcohol [2].

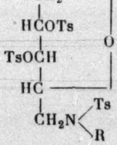
We studied the reaction of xylitan chlorohydrin with various amines and prepared the previously unknown compounds: 5-amino-1,4-anhydroxylitol (I), 5-ethylamino-1,4-anhydroxylitol (II), 5-diethylamino-1,4-anhydroxylitol (III), 5-phenylamino-1,4-anhydroxylitol (IV) and 5-piperidino-1,4-anhydroxylitol (V).

The amines were characterized as their tosyl derivatives, which we used for subsequent syntheses.

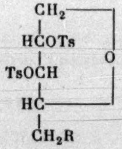


R = NH_2 (I), NHC_2H_5 (II), $N(C_2H_5)_2$ (III), NHC_6H_5 (IV), $N(CH_2)_5$ (V).

p-Toluenesulfonyl chloride reacted with the alcohol groups producing esterification (compounds VI–X) and also with the amino groups for the primary (I) and secondary (II and IV) amines, forming substituted sulfonamides (VI–VIII).



R = H (VI), C_2H_5 (VII), C_6H_5 (VIII).



R = $N(C_2H_5)_2$ (IX), $N(CH_2)_5$ (X),
Ts = $O_2SC_6H_4CH_3$-*n*.

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[*] This article is the 7th in the series "Anhydrides and amino- and guanido-derivative of carbohydrates and polyhydric alcohols;" for the 6th report see J. Gen. Chem. 28, 3206 (1958) [preceding article].

TABLE 1

Preparation Conditions, Properties and Analyses of Xylitan Amino Derivatives

Exp. No.	Amino derivative	Reaction conditions	Yield (in %)	Melting point or boiling point	n_D^{20}	Found (in %)				Calculated (in %)			
						C	H	N	Cl	C	H	N	Cl
1	Aminoxylitan hydrochloride $C_5H_{12}O_3NCl$ (I)	100—110° 25 hours	37.3	133—134°	—	35.90, 36.03	7.43, 7.46	8.27, 8.34	21.11, 21.21	35.70	7.09	8.21	20.91
2	Ethylaminoxylitan $C_7H_{15}O_3N$ (II)	120° 72 hours	31.4	130 (1 мм)	1.4908	52.05, 52.40	9.51, 9.70	8.28, 8.51	—	52.15	9.38	8.69	—
3	Diethylaminoxylitan $C_9H_{19}O_3N$ (III)	120° 72 hours	51	127 (1 мм) 153—155 (5 мм)	1.4823	56.64, 56.69	10.43, 10.11	7.41, 7.47	—	57.12	10.11	7.40	—
4	Phenylaminoxylitan $C_{11}H_{15}O_3N$ (IV)	105° 20 hours	36	134—135	—	62.95, 63.25	7.58, 7.43	6.95, 7.08	—	63.23	7.52	6.69	—
5	Piperidinoxylitan $C_{10}H_{19}O_3N$ (V)	100° 17 hours	46	115—116	—	59.41, 59.58	9.48, 9.36	6.82, 6.80	—	59.85	9.47	6.93	—

TABLE 2

Tosyl Esters of Xylitan Amino Derivatives

Exp. No.	Tosyl derivatives	Melting point	Yield (in %)	Found (in %)				Calculated (in %)			
				C	H	N	S	C	H	N	S
1	(Ditosylxylitanyl)-toluenesulfonamide $C_{26}H_{30}O_9S_3N$ (VI)	146—147°	57.5	—	—	2.27, 2.50	15.60	—	—	2.35	16.15
2	(Ethylditosylxylitanyl)-toluenesulfonamide (VII) $C_{28}H_{34}O_9S_3N$	120—121	50	—	—	2.27, 2.12	15.51, 15.28	—	—	2.24	15.40
3	Ditosyl ester of diethylaminoxylitan $C_{23}H_{32}O_7S_2N$ (IX)	154—155	61	55.48, 55.51	6.44, 6.19	2.39, 2.33	12.86, 12.77	55.40	6.47	2.81	12.85
4	(Phenylditosylxylitanyl)-toluenesulfonamide $C_{32}H_{33}O_9S_3N$ · (VIII)	141—142	87	—	—	1.93, 1.96	14.22, 14.62	—	—	2.09	14.32
5	Ditosyl ester of piperidinoxylitan $C_{34}H_{31}O_3S_2N$ (X)	130—132	41	—	—	—	12.33, 12.25	—	—	—	12.55

We are very grateful to Professor S. N. Danilov, under whose direction the work was performed.

EXPERIMENTAL

Amination of 5-chloro-1,4-anhydroxylitol. Crystalline xylitan chlorohydrin, synthesized by the method we described previously [1], was heated at 100-120° with excess ammonia or amine. We used 40% aqueous ammonia solution and freshly redistilled ethylamine, diethylamine, aniline and piperidine. In the first three cases, the experiments were performed in an autoclave and in the case of aniline and piperidine, in ampoules. The preparation conditions, properties and analyses of the amino derivatives are presented in Table 1. The amino-, ethylamino- and diethylaminoxylitans were sirupy products; the phenylamino- and piperidinoxylitans were crystalline substances.

The amines obtained were readily soluble in water, methyl and ethyl alcohols, acetone, dioxane, piperidine and amines, less soluble in chloroform and dichloroethane and soluble in benzene on heating; they were insoluble in ether.

The reactions gave a mixture of the amino derivative of xylitan and the original amine and their hydrochlorides. Since the properties of these compounds were different, it is better to described the separation conditions and purification of the products for the separate cases.

Aminoxylitan (I). The reaction of xylitan chlorohydrin and ammonia yielded a homogeneous yellow solution from which the ammonia and water were distilled in vacuum. Absolute ethyl alcohol was added to the sirupy residue. After standing for a day, the solution deposited a crystalline precipitate, which was recrystallized 3 times from absolute ethyl alcohol to give aminoxylitan hydrochloride. Hydrogen chloride was passed through the filtrate after separation of the crystals to give an additional portion of the salt. Aminoxylitan (I) was isolated from the salt by treatment with soda in absolute methyl alcohol and formed a sirup, which could not be distilled in vacuum.

Diethylaminoxylitan (III). The reaction mixture after treatment of the chlorohydrin with diethylamine was diluted with dry dioxane and shaken on a mechanical shaker with alkali. The sirup left after evaporation of the dioxane was vacuum-distilled twice.

Ethylaminoxylitan (II). This product was isolated similarly to diethylaminoxylitan.

Phenylaminoxylitan (IV). When the dark-red homogeneous solution from the reaction with aniline was cooled, it was converted into a crystalline mass, mixed with tar. The crystalline part was filtered off and washed with dry ether. The ether-aniline solution gave a second portion of crystals. After isolation of the amino derivative from its salt with soda, the product was recrystallized three times from dichloroethane or chloroform.

Piperidinoxylitan (V). In the case of reaction with piperidine, the piperidine hydrochloride was filtered off from the reaction mixture after heating. Removal of the piperidine in vacuum left a mixture of piperidinoxylitan and its hydrochloride. The residue was recrystallized from benzene, treated with soda in dioxane and recrystallized twice from benzene, when it corresponded in analysis to piperidinoxylitan (V).

Tosylation of xylitan amino derivatives. The amino derivatives were tosylated by the usual method at room temperature in pyridine. In the cases of amino- and phenylaminoxylitan, the oil, precipitated on pouring the reaction mixture into ice water, crystallized rapidly. The crystals were carefully washed free from pyridine and recrystallized from ethyl alcohol. The properties and analyses are presented in Table 2.

In other cases, more complex treatment was required to obtain a crystalline product. Thus, in the case of diethylaminoxylitan, the oil was twice dissolved in methyl alcohol and precipitated with water, then extracted with chloroform, the solution dried over sodium sulfate, the chloroform distilled off and the residue crystallized on standing in a desiccator for two weeks. The ditosyl ester of diethylaminoxylitan was recrystallized from aqueous ethyl alcohol.

SUMMARY

1. A study was made of the reaction of 5-chloro-1,4-anhydroxylitol with ammonia, ethylamine, diethylamine, aniline and piperidine.

2. Previously unknown amino derivatives of xylitan and their tosylation products are described.

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A SEARCH FOR NEW METHODS OF SYNTHESIZING CELLULOSE ETHERS

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The preparation of partially substituted methyl and ethyl ethers of cellulose requires a high expenditure of dialkyl sulfates; in addition, dialkyl sulfates are noxious materials. In connection with this it seemed interesting to search for new alkylating agents which could be used for a substantial modification of the cellulose alkylation process.

It is known that esters of p-toluenesulfonic acid have a high reactivity, making it possible to use them for alkylating amines [1], mercaptans, thiophenols [2] and phenols [3].

The methyl and ethyl esters of p-toluenesulfonic acid were used for the alkylation of cellulose, but the properties of the cellulose ethers obtained were not described [4].

We investigated the possibility of alkylating cellulose both with esters of p-toluenesulfonic acid and with esters of toluenedisulfonic acid, benzenesulfonic acid and α-naphthylenesulfonic acid.

Alkylation with these esters proceeds by the scheme

$$RSO_2OR_1 + (C_6H_{10}O_5)_n \rightarrow [C_6H_{10-x}O_{5-x}(OR_1)_x]n,$$

where : $R = C_6H_5, CH_3C_6H_4, C_{10}H_7, R_1 = CH_3, C_2H_5, n\text{-}C_3H_7, n\text{-}C_4H_9, C_6H_5.$

The alkylation was performed with alkali cellulose, cellulose, dissolved in 35.5% triethylbenzylammonium hydroxide, and hydrocellulose, dissolved in 9-10% sodium hydroxide.

Negative results were obtained in all cases in the alklation of alkali cellulose. The alkylation of cellulose, dissolved in the organic base, proceeded more rapidly than with solutions in alkali; thus, with an alkylation in alkali solution, it was only possible to introduce 3-10% of methyl or ethyl residues, while with an alkylation in an organic base solution, the content of residues reached 12 to 35%. In the alkylation of cellulose in alkali solution with esters of benzenesulfonic acid, it was found that the methyl ester reacted more readily than the ethyl and the ethyl more readily than the propyl, etc.

On the basis of the experimental material, the esters of benzenesulfonic acid may be arranged in the following series according to the case of their substitution reactions:

$$C_6H_5SO_2OCH_3 > C_6H_5SO_2OC_2H_5 > C_6H_5SO_2\,n\text{-}OC_3H_7 \text{ etc.}$$

We were unable to obtain such a series for the same esters in the alkylation of cellulose in the organic base solution, as the reaction proceeded more vigorously.

A comparison of the substitution capacity of the ethyl ester of p-toluenesulfonic acid with the diethyl ester of toluenedisulfonic acid in the etherification of cellulose in an organic base showed that the monoester was more reactive than the diester.

EXPERIMENTAL

(With the participation of F. G. Khavgina)

The esters of the sulfonic acids were prepared from the acid chlorides of the sulfonic acids and alcohols by the method of Izmail'skii and Razorenov [3], with the exception of the phenyl ester of benzenesulfonic acid, which was prepared by heating equimolecular amounts of sodium phenolate and benzenesulfonyl chloride in a

TABLE 1

Alkylation of 2.5% Hydrocellulose Solution (Cu number, 9.3) in 9.50% NaOH Solution with a Molecular Ratio of Ester to Cellulose of 6 : 1

Exp. No.	Alkylating reagent	Reaction temperature	Time (in hours)	OCH_3, OC_2H_5 (in %)	Degree of substitution	Ester recovered (moles)
1	$C_6H_5SO_2OCH_3$	18—20°	2.0	1.47	0.09	4.31
2		30 ± 2	2.0	3.71	0.24	3.65
3		50 ± 2	2.0	10.55	0.69	—
4	$C_6H_5SO_2OC_2H_5$	50 ± 2	2.0	2.95	0.16	2.50
5		70 ± 2	2.0	7.81	0.40	—
6	$C_6H_3SO_2$n -OC_3H_7	50 ± 2	2.0	None	None	4.55
7	$C_6H_5SO_2$n -OC_4H_9	70 ± 2	2.0	None	None	3.91
8	$CH_3C_6H_4SO_2OCH_3$	50 ± 2	4.0	8.09	0.53	—
9		70 ± 2	4.0	5.95	0.40	—
10	$CH_3C_6H_4SO_2OC_2H_5$	50 ± 2	4.0	Traces	None	4.62
11		70 ± 2	4.0	7.76	0.41	Traces
12	$C_{10}H_7SO_2OC_2H_5$	70 ± 2	2.0	Traces	None	4.77

TABLE 2

Alkylation of 2.5% Cellulose Solution in 35.5% Organic Base Solution with a Molecular Ratio of Ester to Cellulose of 6 : 1

Exp. No.	Alkylating reagent	Reaction temperature	Time (in hours)	OCH_3 OC_2H_5 (in %)	Degree of substitution
1	$C_6H_5SO_2OCH_3$	55 — 60°	0.5	16.93	1.11
2	$C_6H_5SO_2OC_2H_5$	50 ± 2	3.0	35.30	1.89
3	$C_6H_5SO_2$n -OC_3H_7	50 ± 2	1.0	—	1.13
4	$C_6H_5SO_2$n -OC_4H_9	50 ± 2	2.0	—	1.11
5	$CH_3C_6H_4SO_2OCH_3$	50 ± 2	3.0	21.50	1.41
6	$CH_3C_6H_4SO_2OC_2H_5$	50 — 60	3.0	34.36	1.85
7		70 — 80	3.0	33.34	1.80
8	$CH_3C_6H_3(SO_2OC_2H_5)_2$	50 — 55	4.0	Traces	None
9	$C_{10}H_7SO_2OC_2H_5$	65 — 70	4.0	12.61	0.67
10	$C_{10}H_7SO_2OC_2H_5$	18 — 20	1.0	23.19	1.24

benzene medium at 35-40° for 8 hours. The sulfonic esters obtained were used for the synthesis of cellulose ethers. In the first series of experiments the cellulose was alkylated in 9.5% sodium hydroxide solution. First of all, samples of hydrocellulose were prepared by solution in 85% phosphoric acid [5]. The moist hydrocellulose (Cu number, 9.3) was dissolved in 9.5% sodium hydroxide at room temperature, then the solution was heated to 30, 50 and 70°, 6 moles of the alkylating reagent added and the reaction performed for 1-4 hours (Table 1).

In the second series of experiments, the alkylation was performed in a 35.5% solution of triethylbenzylammonium hydroxide. The cellulose was dissolved in the organic base at room temperature, then the solution heated to 50-80° and 6 moles of alkylating reagent added to it; the reaction proceeded for 0.5 – 4 hours (Table 2). At the end of the reaction in both the first and the second series of experiments, the unreacted ester was isolated by ether extraction and the unreacted portion determined (Table 1). The aqueous layer was heated to boiling and this coagulated the cellulose ether, which was purified by the usual method.

The cellulose ethers obtained in the first series of experiments were in the form of powders, while the second method gave cellulose ethers as a flocculent mass.

A comparison of experiments 3, 5 and 7 (Table 1) shows that under the same conditions, the alkylating capacity of esters of benzenesulfonic acid falls with an increase in the alkyl radical and similarly for the esters of p-toluenesulfonic acid as shown in experiments 9 and 11.

The alkylation of cellulose in alkali solution gave a methylcellulose (Exp. 3, Table 1), which dissolved in 2-4% sodium hydroxide solution giving a low-viscosity, clear solution.

The data in Table 2 show that in the alkylation of cellulose in the organic base, all the alkylating reagents, with the exception of diethyl toluenedisulfonate, rapidly form cellulose ethers. In experiments 1, 5 and 10 (Table 2), we obtained water-soluble methyl and ethyl ethers of cellulose, which gave very viscous, clear solutions. The propyl and butyl ethers of cellulose only swelled in an alcohol-benzene solution.

Comparison of the experiments performed under the same conditions (Tables 1 and 2) shows that in the organic base solution the alkylation proceeds more completely than in the alkali solution, which is caused by the different natures of sodium hydroxide and the organic base.

SUMMARY

1. Cellulose was alkylated in solutions of alkylated in solutions of alkali and an organic base with the methyl and ethyl esters of p-toluenesulfonic acid, the diethyl ester of toluenedisulfonic acid, the methyl, ethyl, n-propyl and n-butyl esters of benzenesulfonic acid and the methyl and ethyl esters of α-naphthalenesulfonic acid.

2. The medium was shown to have an effect on the transfer of the radical in the etherification of cellulose in solution.

3. It was established that in an alkali solution the ease of alkylation with benzenesulfonic esters fell from methyl to ethyl to n-propyl,etc.

4. It was found that the introduction of a second alkyl group into the monoester of toluenesulfonic acid considerably lowered the capacity of the ester toalkylate cellulose.

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COMPARATIVE DISTRIBUTION OF CARBON DISULFIDE IN THE MAIN AND SIDE REACTIONS IN THE PREPARATION OF VISCOSE AT LOW TEMPERATURE AND UNDER NORMAL CONDITIONS

E. A. Abramova

Many publications have pointed out the relation between the physicomechanical properties of viscose fibers, the degree of substitution of the xanthate and the uniformity of distribution of the ester groups along the chain [1]. The greater the number of ester groups in the xanthate and the higher the uniformity of their distribution, the more homogeneous is the structure of the fibers.

TABLE 1

Amount of carbon disulfide added (in %)	Low temperature conditions (γ)	Normal temperature conditions (γ)
15	27—28	—
20	35	30
30	40—41	35—36
38	58—62	46—48
40	65—66	50—52

Our previous work [2, 3] showed that viscose formation under low-temperature conditions gave a more advantageous distribution of carbon disulfide as regards ester formation with a low consumption of carbon disulfide.

In the present work an examination was made of the comparative distribution of carbon disulfide at two temperatures (low temperature and that normally used) with 15, 20, 30, 38 and 40% of carbon disulfide used. All the experiments were performed on one sample of original cellulose.

(Under low temperature conditions, the alkali cellulose preparation and one third of the sulfidation time was at a temperature of 0 to +5°. The xanthated fibers were dissolved at − 5 to −7°. Under normal conditions, the viscose is formed at from + 15 to + 30°). The solutions obtained were analyzed for composition, degree of substitution (γ) and the distribution of carbon disulfide between the main and the side reactions. The amount of sulfur in the ester groups and in the side products was determined by decomposition with acid and, in parallel, the degree of substitution of the xanthate was determined by iodometric titration. The sodium sulfide was determined potentiometrically.

Investigations were made on viscose solutions with practically the same α-cellulose content and with various free alkali contents. The tables give only the basic data, established in many experiments.

Table 1 gives the degree of substitution (γ is the number of hydroxyl groups in 100 elementary units of the cellulose macromolecule, substituted with ester groups) of the xanthate in the viscose solutions obtained, with a total alkalinity of 7.1-7.3%.

Table 1 shows that in viscose formation at low temperatures with the same amounts of carbon disulfide added, esters with higher degrees of substitution were obtained.

Table 2 gives data on the distribution of xanthate sulfur and side-product sulfur for the two viscose formation conditions with the same viscose solutions. The difference in the distribution values is very clear; moreover, the lower the amount of carbon disulfide introduced into the reaction, the more advantageous is the distribution.

If the concentration of alkali in the viscose is not 7.1-7.3%, as in experiments in Tables 1 and 2, but only 5-6%, then the reduction in the free alkali in the viscose solution has a considerable effect on carbon disulfide distribution, increasing the degree of esterification of the xanthate. The corresponding data are given in Table 3.

TABLE 2

Amount of carbon disulfide added (in %)	Distribution of S (in %)			
	xanthate S	side product S	xanthate S	side product S
	Low temperature conditions		Normal conditions	
15	88	12	—	—
20	82	18	—	—
30	79	21	74	26
38	77	23	64	36
40	76	24	61	39

TABLE 3

Amount of carbon disulfide added (in %)	Distribution of S (in %)		γ	Distribution of S (in %)		γ
	xanthate S	side product S		xanthate S	side product S	
	Low temperature conditions			Normal conditions		
15	87	13	28	—	—	—
30	85	15	44	—	—	—
38	82	18	65	68	32	54
40	79	21	80	66	34	55

TABLE 4

Amount of carbon disulfide added (in %)	Distribution of S (in %)		γ	Distribution of S (in %)		γ
	xanthate S	side product S		xanthate S	side product S	
	Low temperature conditions			Normal conditions		
15	76	24	26	—	—	—
20	77	23	32	72	28	26
30	75	25	34	69	31	31
38	71	29	52	67	33	48
40	70	30	62	66	34	50

The alkali concentration is of great importance in the low temperature process. The water, which is present as ice crystals in capillary spaces in the cellulose fiber, acts as a conductor, when the system thaws out, for the alkaline solution into the newly formed fissures–the intermolecular spaces broadened by the ice. It is possible that with a fall in the alkalinity of the viscose solutions, there is further esterification of the hydroxyl groups which become available due to the larger amount of frozen, and then thawed, water.

We also performed experiments without cooling the alkali cellulose before sulfidation as specified for the low-temperature conditions. By preparing the alkali cellulose at a temperature of 0 to +2° and cooling it to the same temperature before sulfidation, it is possible to improve considerably the swelling and activation of the cellulose. We should also note that at the beginning of sulfidation at these temperatures there was a considerable decrease in the formation of viscose antistabilizers. With low temperature solution, the dispersion of the xanthated fibers was improved.

Table 4 shows data on the distribution of carbon disulfide between the main and the side reactions under the two sets of conditions without the cooling of the alkali cellulose and the initial low-temperature sulfidation, for viscoses with a total alkali content of 7-7.1%.

Excluding the cooling of the alkali cellulose and the low-temperature sulfidation had a considerable effect on the distribution of carbon disulfide and, consequently, on the degree of substitution of the xanthate, which was decreased. However, the effect of low temperature solution was clearly marked.

Using low temperature conditions, it is possible to prepare stable viscoses by dissolving xanthated fiber in water. The viscose solutions obtained have a satisfactory degree of substitution, good viscosity curves with a minimum after 15-20 hours and a high degree of purity (according to comparative photometry).

It is not advantageous to reduce the total alkalinity of the viscose solutions below 4.5-5% as at lower alkali concentrations, hydrolysis of the xanthate ester is accelerated and the sulfur distribution is displaced towards the formation of side products.

SUMMARY

1. When the general method of cellulose activation by low temperatures is used for viscose formation, the reaction equilibria are displaced towards the formation of cellulose xanthate.

2. Using low-temperature conditions and from 15 to 40% of carbon disulfide, it is possible to prepare xanthates with a degree of substitution of from 25 to 80, when under normal conditions the degree of xanthation is from 35 to 50.

3. With a decrease in the alkalinity of the viscose solutions, the distribution of carbon disulfide between the main and the side reactions is displaced towards the formation of cellulose ester.

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INVESTIGATIONS IN THE FIELD OF CONJUGATED SYSTEMS

XCV. REACTIONS OF PIPERYLENE WITH ITS HYDROCHLORIDE AND WITH THE 1,4-HYDROCHLORIDE OF ISOPRENE*

A. A. Petrov, N. A. Razumova and M. L. Genusov

In previous communications it was shown that various unsaturated chlorides of the allyl type react with diene hydrocarbons in the presence of $SnCl_4$ and $ZnCl_2$ to form mixtures of telomers [1]. The amount of products of simple addition of the halogen derivatives to the dienes (in the ratio 1:1) in this mixture depended, in the first instance, on the nature of the halogen derivative and the direction of the addition was determined by the structure of the diene hydrocarbon.

In the present work, this rule was confirmed on new examples. The reaction of piperylene with its hydrochloride (2-chloropentene-3) could be readily stopped at the formation of the substance $C_5H_9-C_5H_8Cl$, while in the reaction of the same diene with an isomeric chloride, the 1,4-hydrochloride of isoprene (1-chloro-3-methylbutene-2), considerably larger amounts of higher telomers were formed under the same conditions. In both cases, the ratio between the simple adducts and the higher telomers depends on the extent of telomerization.

Thus, it was established that with primary halogen derivatives of the allyl type there is a greater degree of telomerization than with secondary derivatives.

As a result of adding 2-chloropentene-3 to piperylene with a degree of telomerization of the order of 35-70%, we obtained predominantly a substance which distilled in vacuum over a 1° range. The amount of higher telomers was 15-35% of the total mixture.

The structure of the constant-boiling substance refered to above was established in the following way.

1. According to analysis data it had the formula $C_{10}H_{17}Cl$ and contained not less than 90% of diene (Kaufman's method) and a readily hydrolyzable chlorine atom.

2. In ozonlysis it gave acetic, α-chloropropionic and methylsuccinic acids. The latter was isolated in about 80% yield.

3. When hydrogenated over Pd/$CaCO_3$ it formed 4-methylnonane.

4. It underwent the Sommelet reaction to the extent of 12% after 6 hours and 25% after 100 hours. The residue after the Sommelet reaction had the properties of the original chloride. After a further treatment with urotropine for 100 hours, the material did not change its properties also and over 6 hours, it reacted further with urotropine (in an analytical determination) to the extent of 11%. These data indicate the relative individuality of the product.

As a result of the Sommelet reaction, we obtained a carbonyl compound in a total yield of 5.4% on the chloride taken and 24% on that reacted. The substance had an unpleasant, obtrusive smell. Its infrared spectrum showed bands characteristic of conjugated double bonds (1632 cm^{-1}), the group $-CH=CH-$ (973 cm^{-1}) and a conjugated carbonyl group (1688 cm^{-1}). In the region of 2730 cm^{-1}, the substance absorbed very weakly, indicating that aldehydes were absent or only present in insignificant amounts.

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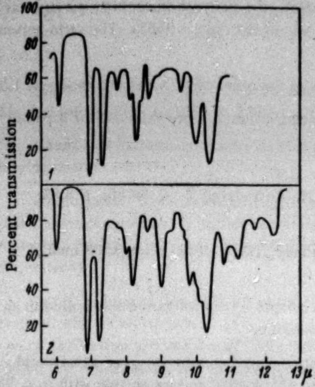
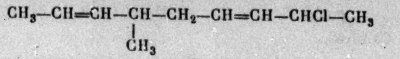
*Diene compounds. LXXI. Reactions of Dienes with Halogen Derivatives. VII.



Infrared absorption spectra of telomerization products of 2-chloropentene-3 (1) and 1-chloro-3-methylbutene-2 (2) with piperylene.

5. The infrared spectrum of the chloride investigated had intense frequencies of the group $-CH=CH-$ (1660 and 965 cm^{-1}) but did not contain the frequencies of the vinyl group (920, 980 and about 6100 cm^{-1}).

All these data indicate that the main addition product (more than 80%) of 2-chloropentene-3 to piperylene is 2-chloro-6-methylnonadiene-3,7 (I).



$$CH_3-CH=CH-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH=CH-CHCl-CH_3$$

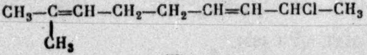
(I)

It was thus established that piperylene adds its hydrochloride in the 1,4-positions, i.e., in the same way as hydrogen halides. The particular tendency of piperylene for 1,4-addition is apparently due to its high polarity (dipole moment 0.68 D).

In the reaction of piperylene with the 1,4-hydrochloride of isoprene (prenyl chloride) with telomerization to the extent of about 75%, we obtained very little of the primary telomerization products. With about 25% telomerization, the yield of the latter was raised to 40% of the total telomer mixture, but we were unable to isolate discrete substances by distillation. To establish the structure of the main substance, we worked with a fraction boiling over a range of 10°. We thus obtained the following data.

1) The mixture investigated had the composition $C_{10}H_{17}Cl$ and did not contain less than 80% of a diene halogen derivative (Kaufman's method). About 90% of the chlorine was readily hydrolyzable. 2) During ozonolysis it formed acetone and α-chloropropionic and succinic acids. 3) On hydrogenation over $Pd/CaCO_3$ it gave a hydrocarbon with a boiling point close to that of 2-methylnonane, but slightly higher specific gravity and refractive index. 4) In the Sommelet reaction, 23% of the material reacted after 100 hours. 5) The infrared spectrum showed a double-bond frequency of 1670 cm^{-1}, the frequency of the group $-CH=CH-$ at 970 cm^{-1} and the frequency of the group $C=CH-$ at 822 cm^{-1} (all of high intensity). The spectrum also showed the frequencies of a vinyl group (929, 990 and 6100 cm^{-1}), but they were weak (figure).

These data indicate that the main component of the chlorides investigated may be represented by the formula of 8-chloro-2-methylnonadiene-2,6 (II).



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2-CH_2-CH=CH-CHCl-CH_3$$

(II)

Thus, like the hydrochloride of piperylene, the hydrochloride of isoprene adds to piperylene predominantly in the 1,4-position. The nature of the impurity containing a vinyl group requires an independent study. We cannot exclude the possibility of addition at the double bond of the allyl isomer of the hydrochloride (dimethylvinylchloromethane). It is also possible that the impurities are products from decomposition during distillation of the dimers of the halogen derivative or higher telomers.

EXPERIMENTAL

Reaction of piperylene with its hydrochloride. To a solution of piperylene and its hydrochloride (0.6 mole of each) in 30 ml of methylene chloride was added 2 ml of a 5% solution of $SnCl_4$ in the same solvent. The mixture was stirred at 10-15° until the specific gravity increased by 0.044 and then the reaction was stopped by the addition of diethylamine. Distillation of the reaction mixture in vacuum gave 35 g of telomers, which corresponded to 32% telomerization. The telomers were separated by distillation into a first fraction (27 g) and higher telomers (7 g). The ratio between these products was 4 : 1;

In a second experiment with the same amounts of starting materials, the increase in specific gravity was 0.062. We obtained 58 g of telomers. The degree of telomerization was of the order of 55%. The ratio between the first fraction and the higher telomers was 2 : 1.

Finally, in a third experiment the degree of telomerization was of the order of 65% and this ratio was 1.2 : 1.

When the first fraction was distilled through a Widmer fractionating column, more than 90% of it passed over at a constant temperature. For this portion we found:

B.p. 78.5° (10 mm), d_4^{20} 0.8928, n_D^{20} 1.4624, MR_D 53.22; calc. 52.31.
Found %: C 69.74; 69.67; H 10.12, 10.04; Cl 20.15. $C_{10}H_{17}Cl$. Calculated %: C 69.55; H 9.92; Cl 20.53.

Infrared spectrum: 965 v.s., 1007 s., 1056 med., 1152 med., 1188 med., 1212 s., 1238 med., 1293 med., 1369 v.s., 1440 v.s., 1660 med and 1765 med., cm^{-1}.

A 92% diene content was found by Kaufman's method. When a sample of the substance was boiled in an aqueous alcohol solution for 2 hours, 98% of the chlorine passed into solution.

5 g of the chloride was taken for ozonization. The normal treatment of the ozonides gave acetic acid (b.p. 40-45° at 50 mm), α-chloropropionic acid (b.p. 75-80° at 5 mm, n_D^{20} 1.4350 and an anilide with m.p. 93°, which corresponds to literature data [3]) and 3 g of methylsuccinic acid (m.p. 108°, mixed melting point 108°).

For hydrogenation we used 15.8 g of the substance and 40 g of $Pd/CaCO_3$ in 120 ml of methyl alcohol. 4885 ml of H_2 (765 mm, 21.5°) was absorbed, corresponding to 71.4%. The hydrogenation products were separated by diluting the distillate from steam distillation with a saturated solution of $CaCl_2$. We obtained 7.5 g of hydrocarbon (fraction with b.p. 165-170°) and 2.6 g of residue. A second distillation of this fraction yielded 4-methylnonane with the following constants:

B.p. 165-166°, d_4^{20} 0.7360, n_D^{20} 1.4140. These data are close to those reported in the literature [4].

When 52.5 g of the substance was shaken for 100 hours with urotropine by Sommelet's method, we obtained a total of 2.5 g of carbonyl compounds with b.p. about 93° (10 mm), d_4^{20} 0.8724 and n_D^{20} 1.4670.

Found %: C 77.70, 77.52; H 10.80, 10.79. $C_{10}H_{16}O$. Calculated %: C 78.90; H 10.60.

The analytical data show that the substance was not completely pure.

Infrared spectrum: 925 w., 973 v.s., 1020 v.w., 1039 v.w., 1100 v.w., 1150 v.w., 1174 w., 1258 v.s., 1369 v.s., 1465. 1465 v.s., 1632 med., 1688 v.s., 2730 w., 2852 w., 2869 s., 2914 v.s., 2955 v.s., and 3022 w., cm^{-1}.

The 2,4-dinitrophenylhydrazone was red and had m.p. 72-73° (from alcohol).

Found %: N 17.18. $C_{16}H_{22}O_4N_4$. Calculated %: N 16.76.

The residue after the Sommelet reaction (40.5 g, 77%) was the original chloride.

B.p. 78.5° (10 mm), d_4^{20} 0.8917, n_D^{20} 1.4624.
Found %: C 69.55, 69.45; H 9.72, 9.92; Cl 20.62. $C_{10}H_{17}Cl$. Calculated %: C 69.55; H 9.92; Cl 20.53.

After a further 100 hours treatment by the Sommelet method, the residue was shown to contain 10.9 and 11.0% of reactive chlorides by an analytical method [2] over 6 hours.

Reaction of piperylene with prenyl chloride. Under the usual conditions and with an increase in specific gravity of 0.035 (about 35% telomerization), 41 g of prenyl chloride and 28 g of piperylene in 40 ml of methylene chloride yielded 24.5 g of a mixture of telomers, which was separated by distillation (5 mm) into a fraction boiling up to 100° (10.5 g) and higher telomers (13 g). The ratio between these products was 1 : 1.25.

With the same amount of starting materials and an increase in the specific gravity of 0.072, we obtained 54 g of telomers. The degree of telomerization was about 75%. Distillation yielded 6.5 g of a fraction with b.p. up to 100° (5 mm) and 47 g of residue. The ratio between these products was 1 : 7.

In a second distillation of the fraction with b.p. up to 100° (5 mm), the bulk of it (more than 60%) passed over in a 10° range. For this part we found:

b.p. 75-85° (10 mm), d_4^{20} 0.9152, n_D^{20} 1.4712 MR_D 52.73; calc. 52.31.
Found %: C 69.57, 69.48; H 9.88, 9.45; Cl 20.55, 20.41. $C_{10}H_{17}Cl$. Calculated %: C 69.55; H 9.22; Cl 20.53.

Infrared spectrum: 762 v.w.,822 med.,858 w.,893 med.,929 med.,970 v.s.,990 w.,1018 med.,1076 w., 1114 s.,1166 w.,1219 s., 1247 w.,1382 v.s.,1456 v.s.,and 1670 s.,cm^{-1}.

Kaufman's method indicated an 80% diene content. The Sommelet – Leets method [2] showed a 23% active chloride content (shaking for 100 hours).

Ozonolysis of the substance (5 g) yielded acetone (2, 4-dinitrophenylhydrazone – m.p. 125°, mixed melting point – same temperature), liquids containing chloroacids with b.p. 75-85° (9 mm) – predominantly α-chloropropionic acid (anilide – m.p. 93°) and succinic acid with m.p. 183° (a mixed sample melted at the same temperature).

In the hydrogenation of 9.5 g of the substance over 35 g of $Pd/CaCO_3$, 2810 ml of H_2 (748 mm, 20°) was absorbed, which corresponds to 68%. Steam distillation of the reaction mixture, salting-out with $CaCl_2$ and subsequent distillation yielded 3 g of hydrocarbon with b.p. 165-167°, d_4^{20} 0.7490 and n_D^{20} 1.4190. For 2-methylnonane, the literature reports the constants [4]: b.p. 167.8°, d_4^{20} 0.7334, n_D^{20} 1.4125.

SUMMARY

1. An investigation was made of the telomerization of piperylene with its hydrochloride (2-chloropentene-3) and the 1,4-hydrochloride of isoprene – (1-chloro-3-methylbutene-2).

2. It was shown that in the first case the products of 1:1 addition were obtained in considerably greater yield than in the second. In both cases the yields depended strongly on the degree of telomerization.

3. The structures of the first addition products (in the ratio 1:1) were established from data on their ozonization, hydrogenation and reactions with urotropine (Sommelet) and also from a study of their infrared spectra.

4. It was shown that in both cases addition of the halogen derivative in the 1,4-position predominated.

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*Original Russian pagination. See C. B. Translation.

CHEMICAL CONVERSIONS OF α-HALO KETONES

VI. THE ACTION OF SODIUM PHENOLATE AND CRESOLATE ON α-BROMOCYCLOHEXANONE

T. I. Temnikova and N. A. Oshueva

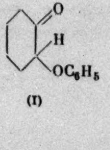
In previous work [1] it was shown that the action of sodium phenolate on aliphatic-aromatic α-bromo ketones yielded different reaction products, depending on the solvent: if the reaction was performed in acetone or ether, α-phenoxy ketones were formed; if the solvent used was methyl alcohol, we obtained the methyl phenyl ketal of the keto alcohol, corresponding to the bromo ketone used. In the latter case, the α-phenoxy oxide (phenyllactolide of the α-keto alcohol) was formed as an intermediate product; however, despite conclusive evidence of its presence in the solution, it was not possible to isolate it in a pure form [2].

In this work, a study was made of the reaction of sodium phenolate and p-cresolate with α-bromocyclohexanone in methyl alcohol; it seemed interesting to determine whether the formation of mixed ketals would be observed in the cyclohexane series: the formation of these would provide indirect evidence of the intermediate formation of phenyllactolides in this series.

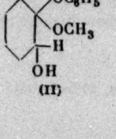
The action of sodium phenolate on α-bromocyclohexanone was first studied in petroleum ether by F. Ebel [3]. In a rapid treatment of the reaction products, he isolated a substance with m.p. 64-65° with the composition $C_{12}H_{14}O_2$. At first Ebel assigned to this the formula of phenoxycyclohexanone; however, having found that the phenoxy group was removed very readily for phenoxy ketones by the action of phenylhydrazine (forming the phenylosazone of cyclohexanolone), indicating a phenoxy oxide, he proposed that the latter was cleaved hydrolytically under the conditions of the reaction with phenylhydrazone to form a keto alcohol. We should, however, note that somewhat earlier, Kötz, in working with α-methoxy- and α-ethoxycyclohexanone, had noted the ease of removal of the alkoxy group under the action of phenylhydrazine [4]. In 1948 the work of Mousseron appeared, in which he prepared authentic phenoxycyclohexanone by oxidation of the monophenyl ether of cyclohexanediol-1,2. The substance melted at 65° [5], like the compound of Ebel; however, the identity of the two substances, melting at the same temperature but prepared by different methods, was not proved.

In the present investigation, we again prepared the substance by Ebel's method, with the difference that the sodium bromide was separated by centrifuging and not washed out with water, to prevent decomposition of the phenyllactolide, if it were otained. The substance obtained, which had m.p. 65°, was examined spectrochemically. The infrared spectrum showed absorption at 1730 cm^{-1} (carbonyl) and at 1588 cm^{-1} (phenyl). It was thus confirmed that α-phenoxycyclohexanone (I) was formed under Ebel's conditions (petroleum ether as solvent). The phenoxycyclohexanone was characterized as the 2,4-dinitrophenylhydrazone. While phenylhydrazine removed the phenoxy group when the phenoxy ketone was heated with phenylhydrazine in acetic acid to give the phenylosazone, 2,4-dinitrophenylhydrazine in sulfuric acid reacted with the carbonyl group only. Separate experiments showed that the phenoxy ketone was stable in hot acetic acid solution (95%) and was not hydrolyzed.

Treatment of α-bromocyclohexanone in methyl alcohol with sodium phenolate gave the methyl phenyl ketal of cyclohexanolone (II).



(I)



(II)

Immediately after vacuum-distillation, the methyl phenyl ketal appeared as a colorless, immobile liquid with a sharp, characteristic smell, slightly reminiscent of the smell of phenol (it did not give a reaction for free phenol with $FeCl_3$). The substance was very unstable; under prolonged heating in vacuum it partly decomposed; therefore, for isolation in an analytically pure state, the ketal was rapidly distilled in small portions; even after a few hours in the cold the liquid acquired a pink color, which gradually became dark-yellow and when a sample was treated with ferric chloride, it gave a violet color.

In contrast to the aliphatic-aromatic methyl phenyl ketals, the freshly distilled ketal (II) reduced Fehlings solution on heating, apparently due to ready hydrolysis. The substance was hydrolyzed rapidly when heated with a 5% aqueous alcohol solution of sulfuric acid; the hydrolysis products, phenol and cyclohexanolone, were characterized as triiodophenol and the 2,4-dinitrophenylosazone. We should note that the reaction with 2,4-dinitrophenylhydrazine proceeded rapidly and almost quantitatively; this derivative is better for characterization of cyclohexanolone.

Treatment of α-bromocyclohexanone with sodium p-cresolate in methyl alcohol also gave the methyl p-cresyl ketal of cyclohexanolone. This ketal was also unstable.

The high instability of the methyl phenyl ketal of cyclohexanolone differed sharply from the stability of methyl phenyl ketals of α-keto alcohols of the aliphatic-aromatic series; the latter are crystalline substances, which are stable to storage and not hydrolyzed when heated with Fehling's solution.

EXPERIMENTAL

α-Bromocyclohexanone was prepared by the method of L. A. Ianovskaia and A. P. Terent'ev [6]. The b.p. was 83-86° at 10 mm.*

Preparation of methyl phenyl ketal of cyclohexanolone. 11.2 g of α-bromocyclohexanone was gradually added to a solution of sodium phenolate, prepared from 2.7 g of sodium, 11 g of phenol and 60 ml of methyl alcohol. A precipitate of sodium bromide began to form immediately. Next day the precipitate was separated, the methyl alcohol removed in vacuum and the viscous orange residue freed from residual sodium bromide. Crystallization did not occur, even after long storage. Two vacuum distillations yielded 6 g of ketal with b.p. 70-72° at 5 mm, d_4^{20} 1.089, n_D^{20} 1.5100.

Found %: C 70.28, 69.85; H 8.6, 8.05; OCH_3 14.45, 14.40. M 236. $C_{13}H_{18}O_3$. Calculated %: C 70.27; H 8.10; OCH_3 13.97. M 222.

The methyl phenyl ketal of cyclohexanolone was hydrolyzed by heating for 2 hours with a 5% aqueous alcohol solution of sulfuric acid. The hydrolysis product was made alkaline and extracted with ether in an extractor. After evaporation of the ether, the residue partially crystallized. The whole oily reaction product was treated with a sulfuric acid solution of 2,4-dinitrophenylhydrazine. A voluminous, bright-red precipitate of the 2,4-dinitrophenylosazone of cyclohexanolone formed. The m.p. was 224-225°. A mixture with an authentic sample melted at the same temperature.

Found %: N 23.53. $C_{18}H_{16}O_8N_8$. Calculated %: N 23.72.

Preparation of methyl p-cresyl ketal of cyclohexanolone. 24 g of bromo ketone was added to a solution of sodium p-cresolate, prepared from 3.3 g of Na, 15.3 g of p-cresol and 55 ml of methyl alcohol. The reaction mixture was treated in the usual way, the ether solution washed with alkali and the product vacuum-distilled twice to give a substance with b.p. 90° at 10 mm, n_D^{20} 1.5005; d_4^{20} 1.061.

Found %: C 71.08, 71.20; H 8.34, 8.46; OCH_3 12.75. $C_{14}H_{20}O_3$. Calculated %: C 71.18; H 8.47; OCH_3 13.13.

Preparation of 2,4-dinitrophenylhydrazone of α-phenoxycyclohexanone. The α-phenoxy ketone was prepared by Ebel's method. A hot alcohol solution of the phenoxy ketone was added to an alcohol-sulfuric acid solution of 2,4-dinitrophenylhydrazine; the 2,4-dinitrophenylhydrazone began to precipitate immediately. The product was recrystallized from ethyl alcohol. The m.p. was 149-150°.

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*Note added during proofreading. All our experimental data show that despite the statement of L. V. Machinskaia and A. S. Podberezina [J. Gen. Chem. 28, 1501 (1958)], α-bromocyclohexanone may be prepared in good yield by the method of Ianovskaia and Terent'ev.

Found %: N 15.23, 15.44. $C_{18}H_{18}O_5N_4$. Calculated %: N 15.14

SUMMARY

Treatment of α-bromocyclohexanone with sodium phenolate and p-cresolate in methyl alcohol gave methyl phenyl and methyl cresyl ketals of cyclohexanolone.

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AN INVESTIGATION OF THE CONVERSIONS OF SECONDARY-TERTIARY α-GLYCOLS OF THE ACETYLENE SERIES UNDER THE ACTION OF MERCURY SALTS

III. 2-METHYL-1,4-DIPHENYLBUTYNE-3-DIOL-1,2

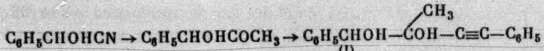
A. Fabritsy and E. D. Venus-Danilova

Previously one of us and V. M. Al'bitskaia [1, 2] established that, when treated with an alcohol solution of mercuric chloride, secondary-tertiary acetylene α-glycols (diphenyl-phenylacetyleneylethylene glycol and dimethyl-phenylacetylenylethylene glycol) gave good yields of the corresponding furans (2,3,5-triphenyl- and 2,3-dimethyl-5-phenylfurans).

The same results were obtained by L. A. Pavlova [3] on treating a primary-secondary acetylene α-glycol (phenyl-phenylacetylenylethylene glycol) with mercuric chloride and also with an alcohol solution of sulfuric acid. In both cases 3,5-diphenylfuran was isolated, but in the reaction with sulfuric acid, simultaneously with the substituted furan, the partial ethyl ether of the original glycol – 2-ethoxy-2,4-diphenylbutyn-3-ol-1 – was obtained.

In the present work we present the results of reacting another secondary-tertiary α-glycol of the acetylene series – 2-methyl-1,4-diphenylbutyne-3-diol-1,2 (I) – with mercuric chloride and sulfate in alcohol. In contrast to those examined previously, the molecule of this glycol contains a different type of substituent (aryl and alkyl) at the carbon atoms bearing hydroxyls.

The glycol was synthesized by the method of Iotsich from phenylacetylcarbinol and phenylacetylenylmagnesium bromide. The phenylacetylcarbinol was prepared by treating mandelonitrile with methylmagnesium bromide according to literature data [4].



$$C_6H_5CHOHCN \rightarrow C_6H_5CHOHCOCH_3 \rightarrow C_6H_5CHOH-\overset{CH_3}{C}OH-C\equiv C-C_6H_5$$

(I)

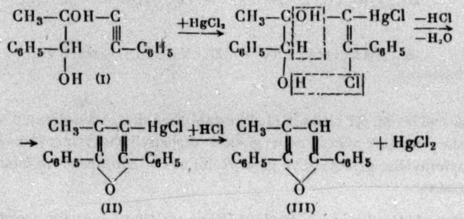
Considering the investigations of T. I. Temnikov [5] on the interconversions of methylbenzoyl- and phenylacetylcarbinols under the action of methylmagnesium bromide and phenylmagnesium bromide, we might expect that the synthesis of 2-methyl-1,4-diphenylbutyne 3-diol-1,2 would also give some of the isomeric 3,5-diphenylpentyne-4-diol-2,3 if the starting phenylacetylcarbinol were isomerized under the action of the phenylacetylenylmagnesium bromide. However, we isolated a single, normal reaction product, and the homogeneity of the glycol synthesized was confirmed by the products of its oxidation with lead tetraacetate – benzaldehyde and methyl phenylacetylenyl ketone – and the preparation from it of 3-methyl-2,5-diphenylfuran, which is described in the literature [6, 7], and not the isomeric 2-methyl-3,5-diphenylfuran.

When treated with an alcoholic solution of mercuric chloride, the 2-methyl-1,4-diphenylbutyne-3-diol-1,2 very rapidly formed a voluminous, white, silky precipitate, which gradually dissolved on heating so that the final reaction product was 3-methyl-2,5-diphenylfuran [6, 7] (III). The formation of a curdy precipitate and its gradual solution were also observed in the treatment of a primary-tertiary acetylene α-glycol with an alcohol solution of mercuric chloride [3].

It was found that the crystalline precipitate formed during the reaction of 2-methyl-1,4-diphenylbutyne-3-diol-1,2 with mercuric chloride contained chlorine and mercury and corresponded in properties and analysis data (Calculated %: Hg 42.88; Cl 7.59) to mercurated 3-methyl-2,5-diphenylfuran (II). The possible hypothesis that the organomercury compound was the product of the addition of mercuric chloride at the triple bond has to be rejected as in this case the substance should contain less mercury and more chlorine (Calculated %: Hg 38.38; Cl 13.58).

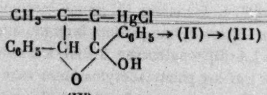
The organomercury compound obtained was quite stable in neutral solution, did not change when boiled with alcohol and water and was converted into the substituted furan only when hydrochloric acid was added and the mixture heated.

On the basis of the data obtained, it is reasonable to assume that the conversion of secondary-tertiary α-glycols of the acetylene series under the action of mercuric chloride into the substituted furans proceeds through mercurated furans by the following scheme:



We should note that the amount of hydrochloric acid determined in the solution after separation of the mercurated furan (II) corresponded exactly to the theoretical if the starting glycol and mercuric chloride were taken in equimolecular amounts (1:1). Changing the ratio of glycol to mercuric chloride so that the amount of mercuric chloride was decreased (1:0.5) had little effect on the yield of substituted furan (III), as was noted in previous investigations [1-3]. Evidently, the mercuric chloride obtained by thermal decomposition of the mercurated furan (II) may again react with glycol, if the latter is in excess of the mercuric chloride.

The proposed mechanism for the formation of substituted furans from secondary-tertiary acetylene α-glycols under the action of mercuric chloride explains the role of the mercuric chloride in this reaction. However, if we consider the formation of a mercurated ethylene γ-keto alcohol in the reaction of an unsymm. dimethyl-phenyl-phenylacetylenylethylene glycol with mercury salts [8, 9], we could suppose that substituted furans also are obtained from secondary-tertiary acetylene α-glycols by the method proposed previously [8], namely through the stage of allene rearrangement of the addition product of the mercury salt to the glycol with the formation of a mercurated ethylene γ-keto alcohol and cyclization of this into the mercurated hydroxydihydrofuran (IV). On losing water, the latter gives the mercurated furan (II), which is converted into substituted furan (III) by the action of hydrochloric acid.



(IV)

However, the second scheme is less probable than the first.

When 2-methyl-1,4-diphenylbutyne-3-diol-1,2 was heated with mercuric sulfate in alcohol, 3-methyl-2,5-diphenylfuran was also isolated, but we have examined neither the intermediate product (mercurated furan) nor the mechanism of this reaction as yet. It is reasonable to assume that in this case, as with mercuric chloride, the first stage is the addition of mercuric sulfate at the acetylene bond of the glycol to form the unstable cyclic organomercury compound. This compound is dehydrated and cyclized to form the β-mercuroorganic compound of furan, which loses mercuric sulfate and is converted into the substituted furan. A similar scheme was proposed by I. N. Nazarov and S. G. Matsoian [10] to explain the cyclohydration of acetylene γ-glycols into furanones in the presence of mercuric sulfate.

EXPERIMENTAL

1. Synthesis of 2-methyl-1,4-diphenylbutyne-3-diol-1,2 (I)

The starting phenylacetylcarbinol was prepared by treating mandelonitrile [4] (34.5% yield on benzaldehyde) with methylmagnesium bromide. The b.p. was 126-128° (16 mm).

For the synthesis of 2-methyl-1,4-diphenylbutyne-3-diol-1,2, we used 9.5 g of magnesium, 38 g of methyl bromide, 37 g of phenylacetylene and 22 g of phenylacetylcarbinol. To the phenylacetylenylmagnesium mide, prepared in the usual way, was added an ether solution of phenylacetylcarbinol over a period of 2 hours with stirring and cooling. When all the phenylacetylcarbinol had been added, the reaction mixture was heated for half an hour so that the ether boiled gently, then, after a day, decomposed with ammonium chloride solution and extracted with ether and the ether extract dried with sodium sulfate. After removal of the ether and phenylacetylene (in vacuum), a thick, sirupy product remained, which crystallized only after prolonged storage. Recrystallization from a mixture of petroleum ether and benzene (5:1) yielded 20 g (54.7%) of a substance with m.p. 82-83°. The substance was readily soluble in ether, benzene and alcohol, difficultly soluble in petroleum ether, decolorized an aqueous solution of potassium permanganate and bromine in chloroform and reacted vigorously with methylmagnesium bromide. When decomposed with potassium carbonate at 260°, the substance gave phenylacetylene, which was detected by the formation of a precipitate with an ammoniacal solution of silver oxide.

Found %: C 81.25, 81.18; H 6.53, 6.54; OH 13.79, M 243.5, $C_{17}H_{14}(OH)_2$. Calculated %: C 80.95; H 6.35; OH 13.49. M 252.

According to analysis data, the substance with m.p. 82-83° was a secondary-tertiary acetylene α-glycol.

Oxidation of the glycol with lead tetraacetate [11]. 5.4 g (20% excess) of lead tetraacetate was added in small portions with stirring to a solution of 2.5 g of the glycol in 25 ml of glacial acetic acid. When all the oxidant had been added, the reaction mixture was heated at 60-65° for 2 hours. After one day, the bulk of the acetic acid was neutralized with an aqueous solution of potassium carbonate and the oxidation product steam-distilled; three fractions of distillate (15-20 ml each) were collected. Each fractions was extracted with ether and the ether extracts were washed with water until neutral and dried with sodium sulfate. Removal of the ether from all the fractions gave small amounts of liquid products.

A 2,4-dinitrophenylhydrazone was prepared under the usual conditions [12] from the liquid of the 1st and 2nd fractions and a semicarbazone from the 3rd fraction.

The 2,4-dinitrophenylhydrazone melted at 186-186.5° (from glacial acetic acid).

Found %: C 58.99, 58.94; H 3.99, 4.00; N 17.12, 17.19. $C_{16}H_{12}O_4N_4$. Calculated %: C 59.26; H 3.70; N 17.28.

In melting point [13] and analysis data, the 2,4-dinitrophenylhydrazone corresponded to that of methyl phenylacetylenyl ketone (1-phenylbutyn-1-one-3).

The semicarbazone had m.p. 221-222° (from alcohol), which corresponded to the m.p. of benzaldehyde semicarbazone and did not depress the melting point of an authentic sample.

Found %: N 25.50, 25.78. $C_8H_9ON_3$. Calculated %: N 25.76.

In addition to the methyl phenylacetylenyl ketone and benzaldehyde, the oxidation products also yielded a very small amount of benzoic acid (mixed melting point) with m.p. 121° (after sublimation).

2. Action of Mercuric Chloride on 2-methyl-1,4-diphenylbutyne-3-diol-1,2

All the experiments were performed in a flask with a reflux condenser and a stirrer at the boiling point of the alcohol, in contrast to the experiments described previously [1, 2], in which the reaction was performed at 100° in sealed tubes.

3 g of glycol and 6.5 g of mercuric chloride (1 mole of glycol to 2 moles of mercuric chloride) were dissolved separately in a total of 45 ml of 95% ethyl alcohol. A minute after the solutions had been mixed, a white, crystalline silky precipitate began to form, the amount rapidly increased and after a short time, the whole mass solidified. When heated for 1 hour, the precipitate almost completely dissolved. The solution was cooled and filtered and the precipitate on the filter (m.p. 230-235°) was not examined more closely due to its small amount (~ 0.1 g). The filtrate was diluted with 200 ml of water and the oily substance liberated was extracted with benzene and dried with sodium sulfate. Removal of the benzene under reduced pressure yielded a solid substance with m.p. 58-59° (from methyl alcohol). The product was readily soluble in benzene and ether, less soluble in alcohol, decolorized a chloroform solution of bromine and an aqueous solution of potassium permanganate on heating and gave a weak blue fluorescence with concentrated sulfuric acid, which disappeared when the solution was diluted with water; the substance gradually became yellow on storing. According to analysis, it did not contain carbonyl or hydroxyl groups and was 3-methyl-2,5-diphenylfuran, which is described in the literature [6, 7]. We obtained 2.4 g (86.2%).

Found %: C 86.92, 86.82; H 5.98, 6.18. M 226.5. $C_{17}H_{14}O$. Calculated %: C 87.18; H 5.99. M 234.

We performed two further experiments under the same conditions with the same amount of glycol, but with different amounts of mercuric chloride – 1 mole and 0.5 mole of mercury salt to 1 mole of glycol. 3-Methyl-2,5-diphenylfuran with m.p. 58-59° was isolated in both cases in 82.6% yield.

In order to investigate the crystalline precipitate initially formed, a 4th experiment was performed with 3 g of glycol and 3.25 g of mercuric chloride (1:1). The reaction mixture was kept at room temperature for 3 days and then the fine, crystalline precipitate was filtered off, washed several times with alcohol and dried in a desiccator. The m.p. was 237-238° (from benzene).

The filtate, diluted with water, (acid reaction) did not contain any organic material; it was found that all the mercuric chloride had reacted, since the filtrate contained only 0.077 g of mercury (as HgS), which corresponds to 0.1 g of mercuric chloride. 0.4342 g of chlorine was found; allowing for the chlorine present in the residual mercuric chloride, this represents 0.408 g of chlorine (or 0.418 g of HCl) liberated as hydrochloric acid in the reaction of the glycol with mercuric chloride. Theoretically, the solution should have contained 0.422 g of chlorine (0.434 g of HCl), which agrees well with the analysis data.

The crystalline substance isolated with m.p. 237-238° contained mercury and chlorine, did not contain hydroxyl groups, sluggishly decolorized a chloroform solution of bromine and an aqueous solution of potassium permanganate, was sparingly soluble in most organic solvents and was not changed on boiling with water.

Found %: Hg 42.45, 42.51; Cl 7.28, 7.39. $C_{17}H_{13}OClHg$. Calculated %: Hg 42.88; Cl 7.59.

The molecular weight was not determined due to the insignificant solubility of the substance in organic solvents.

Judging by the analysis data and the properties, the substance was 3-methyl-2,5-diphenyl-4-chloromercurifuran (II). We obtained 4.9 g (87.8%).

In a special experiment, an examination was made of the crystals precipitated immediately after the alcohol solutions of glycol and mercuric chloride were mixed (after 10-15 minutes). The precipitate was also 3-methyl-2,5-diphenyl-4-chloromercurifuran (II) (m.p. 237-238°).

When 1 g of 3-methyl-2,5-diphenyl-4-chloromercurifuran with alcohol was heated on a boiling water bath for 6 hours, the substance was recovered unchanged. Only when 0.5 ml of hydrochloric acid (d 1.16) was added to the reaction mixture, did the precipitate decompose rapidly. Dilution with water and extraction with benzene yielded 0.49 g (87.3%) of 3-methyl-2,5-diphenylfuran (III) with m.p. 58° from 1 g of mercurated furan (II).

3. Action of mercuric sulfate on 2-methyl-1,4-diphenylbutyne-3-diol-1,2

3 g of the acetylene glycol (m.p. 82-83°), 3.54 g of mercuric sulfate (1 mole : 1 mole) and 50 ml of 80% ethyl alcohol were used. A large part of the mercuric sulfate did not dissolve during mixing and a yellowish precipitate was formed. After being heated for 3 hours on a boiling water bath, the mixture was poured with stirring into 300 ml of water. Removal of the benzene from the extracts yielded 1.74 g (62.5%) of 3-methyl-2,5-diphenylfuran with m.p. 57-58°.

SUMMARY

1. 2-Methyl-1,4-diphenylbutyne-3-diol-1,2, which is not described in the literature, was synthesized and it was shown that when treated with mercuric chloride and sulfate, this glycol formed 3-methyl-2,5-diphenylfuran.

2. When the glycol was treated with mercuric chloride, first there was formed an intermediate product from reaction of the glycol with mercuric chloride – 3-methyl-2,5-diphenyl-4-chloromercurifuran.

3. A mechanism for the conversion of 2-methyl-1,4-diphenylbutyne-3-diol-1,2 into 3-methyl-2,5-diphenylfuran was proposed.

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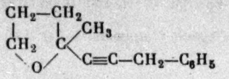
THE MECHANISM OF DEHYDRATION OF γ-GLYCOLS

VI. STUDY OF THE DEHYDRATION OF 3-METHYLHEXYNE-1-DIOL-3,6

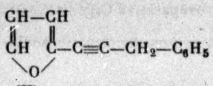
T. A. Favorskaia and O. V. Sergievskaia

In studying the dehydration of γ-glycols, we showed [1-3] that the ethylene alcohols formed as a result of this reaction very readily isomerized into derivatives of tetrahydrofuran, with the exception of 2-phenylpenten-2-ol-5, which contains a system of conjugated bonds in its molecule and was not isomerized into 2,2-methylphenyltetrahydrofuran; the latter was formed from the glycol under considerably more drastic conditions by the elimination of water from the two hydroxyl groups.

With the intention of preparing 2,2-methylbenzylacetylenyltetrahydrofuran (I), an analog of the antibiotic, carlene oxide (II) [7], we synthesized the acetylene γ-glycol, 3-methylhexyne-1-diol-3,6 [4] (III) and studied its dehydration for the preparation of 2,2-methylacetylenyltetrahydrofuran (IV).



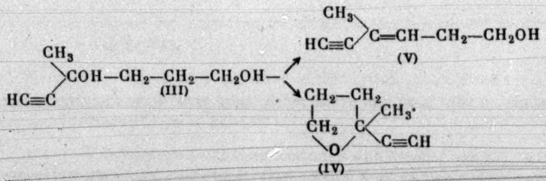
(I)



(II)

In most cases, the many experiments we performed on the dehydration of the glycol (III) gave insignificant yields of (IV) (10-47%) due to the formation of the enyne alcohol (V), which readily polymerized in an acid medium and gave a considerable amount of tar, as was shown previously [5].

The reaction proceeded in two directions:

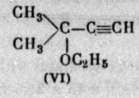


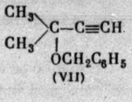
The alcohol (V), 3-methylhexen-3-yn-1-ol-6, was not isomerized into a tetrahydrofuran derivative, due to the presence of a stable system of a conjugated double and triple bond in it. We attempted to isomerize it under more drastic conditions by distillation in the presence of concentrated sulfuric acid; part of the alcohol distilled unchanged and the bulk of it was thus converted into a tarry polymer. The formation of 2,2-methylacetylenyltetrahydrofuran in this case, as in the case of 2,2-methylphenyltetrahydrofuran, may be explained by the elimination of water from the two hydroxyl groups of the glycol.

The structure of 2,2-methylacetylenyltetrahydrofuran was proved by hydrogenating it over platinum black to give 2,2-methylethyltetrahydrofuran, which we had prepared previously [6]. In addition, the structure (II) was confirmed by plotting the Raman and infrared spectra.

Carlene oxide was synthesized in 20% yield by Pfau et al. [7] by the action of benzyl chloride on furylacetylenylmagnesium bromide. We attempted to synthesize 2,2-methylbenzylacetylenyltetrahydrofuran by the action of benzyl bromide on the sodium or potassium derivative of 2,2-methylacetylenyltetrahydrofuran in liquid ammonia. As a result of the reaction, a considerable part of the starting material was recovered unchanged and the rest was converted into a nitrogen-containing substance with m.p. 98°, which we did not examine more closely. An attempt to isolate the sodium derivative of the product (IV) and react it with benzyl bromide in absolute ether was also unsuccessful. It was not possible to prepare the Na-derivative of 2,2-methylacetylenyltetrahydrofuran in boiling xylene, either. It was then decided to determine whether the sodium derivative formed in liquid ammonia was a derivative of 2,2-methylacetylenyltetrahydrofuran. When the reaction product was decomposed with water, part of the starting material was recovered and the other part was converted into a product, which, though it was unsaturated, did not give a precipitate with an ammonia solution of silver oxide and did not absorb in the infrared in the region of 2100-2140 cm^{-1}, characteristic of a triple bond; this product did not contain nitrogen, did not react with 2,4-dinitrophenylhydrazine solution, but reacted vigorously with methylmagnesium iodide. It was thus obvious that under the action of sodium, 2,2-methylacetylenyltetrahydrofuran underwent some deep conversion, which also explained the impossibility of preparing the required tetrahydrofuran derivative in this way.

The conversions of 2,2-methylacetylenyltetrahydrofuran described compelled us to determine how the reaction of sodium and halogen derivatives would proceed with alcohols of the acetylene series — whether this would give ethers, or whether substitution of the acetylene hydrogen by the corresponding radical would occur. With this aim, we studied the reaction of dimethylacetylenylcarbinol with ethyl bromide and benzyl bromide and sodium in liquid ammonia. In the first case we obtained the ethyl ether of dimethylacetylenylcarbinol (VI), which was much lower-boiling than the alcohol, gave a precipitate with an ammonia solution of silver oxide and contained the amount of ethoxyl group required by the formula indicated.


(VI)


(VII)

The reaction of dimethylacetylenylcarbinol with sodium and benzyl bromide gave a substance which had a neutral reaction, did not contain a hydroxyl group, did not give a reaction for an acetylene hydrogen and did not form a precipitate with mercuric chloride solution. The molecular refraction found corresponded with the refraction calculated for the benzyl ether of dimethylacetylenylcarbinol (VII). The presence of a triple bond in the ether obtained was confirmed by plotting the infrared and Raman spectra. The compound obtained was hydrogenated over Pt-black to give the benzyl ether of dimethylethylcarbinol, whose constants agreed well with the literature data.

The acetylene ether obtained was ozonized and gave the normal ozonolysis products, formic and benzyloxyisobutyric acids, but in addition, in one of the experiments we isolated methacrolein and benzaldehyde and in another, methacrolein and benzoic acid. The formation of these products may be explained by oxidative cleavage of the C—O bond.

In addition to the ether described above, the reaction of dimethylacetylenylcarbinol with sodium and benzyl bromide always gave a small amount of a lower fraction, which crystallized on standing. This substance contained 10% of nitrogen, had m.p. 96-98° and did not depress the melting point of the crystalline nitrogen-containing substance obtained previously. The structure of this product was not investigated.

An attempt was made to substitute the acetylene hydrogen in the benzyl ether of dimethylacetylenylcarbinol with sodium and then with ethyl by a reaction in liquid ammonia; however, this attempt was not successful and the ether was recovered unchanged.

EXPERIMENTAL

I. Dehydration of 3-methylhexyne-1-diol-3,6 (III) with sodium bisulfite. This reaction was originally undertaken in connection with the need of purifying the glycol from traces of acetopropyl alcohol, which is the starting material in its synthesis, but in the study of the reaction products, it was found that part of the glycol was dehydrated to form 2,2-methylacetylenyltetrahydrofuran (IV) and the enyne alcohol (V). The yield of the purified glycol was only 28.5%.

35 g of the glycol was shaken with a freshly prepared, saturated solution of sodium bisulfite in a bottle with a ground stopper. The reaction mixture was left overnight, then the reaction products were extracted with ether and dried with Na_2SO_4. Removal of the solvent and distillation of the residue yielded the following fractions: 1st b.p. 125°, 7.5 g; 2nd b.p. 45-60° (26 mm), 2g; 3rd 78-90° (15-19 mm), 8 g; 4th 105-125° (15 mm), 2 g; 5th 130° (15 mm), 10 g.

The 1st and 2nd fractions were combined and distilled on a column. We obtained 6.6 g of 2,2-methylacetylenyltetrahydrofuran.

B.p. 123-124°, n_D^{20} 1.4404, d_4^{20} 0.9117; MR_D 31.78. $C_7H_{10}O$ ₣. Calculated 31.90.
Found %: C 75.64; H 9.24. M 103. $C_7H_{10}O$. Calculated %: C 76.36; H 9.09, M 110.

Due to the extreme volatility of the substance, the elementary analysis was performed several times both by Korshun's method and by Pregl's, but completely satisfactory results could not be obtained.

Hydrogenation of 2,2-methylacetylenyltetrahydrofuran. 1.71 g of the substance was hydrogenated over Pt-black. 697 ml of hydrogen (95% of theoretical, calculated on a triple bond) was absorbed. After removal of the solvent, the substance was distilled over metallic sodium. We obtained 0.2 g of material with b.p. 118-121° and n_D^{20} 1.4220.

According to literature data, 2,2-methylethyltetrahydrofuran has b.p. 118-122° and n_D^{20} 1.4230 [6].

2,2-Methylacetylenyltetrahydrofuran reacted readily in the cold with an ammonia solution of silver oxide.

The structure of 2,2-methylacetyltetrahydrofuran was confirmed by plotting the Raman and infrared absorption spectra. The former was plotted on an ISP-51 apparatus with a slit of 0.06*and an exposure of 5 hours.

The following frequencies (cm^{-1}) were obtained: 618(4), 740(2), 852(3), 922(6), 1004(3), 1100(2), 1171(3), 1234 (broad), 1446 (5), 1483 (3), 2051 (2), 2108 (10), 2870 (broad), 2934 (very broad), 2983 (very broad). The frequency of 2108 cm^{-1} corresponds to the triple bond and the frequency 922(6) cm^{-1} to the vibration frequency of the tetrahydrofuran skeleton ([8].

The infrared absorption spectrum was plotted on an IKS-11 apparatus with an NaCl prism, d 58 μ, from 860 to 1300 cm^{-1} and from 1300 to 2200 cm^{-1} and with an LiF prism, d 15 ± 2 μ, from 2930-3600 cm^{-1}.

The frequency of 3285 cm^{-1} corresponds to the valence oscillation of $\equiv CH$; the frequency of 2120 cm^{-1} corresponds to the valence oscillation of $-C\equiv CH$; 1100 cm^{-1} to valence oscillations of the $C-O-C$ group in the tetrahydrofuran ring [9]; 905 cm^{-1} to the oscillation of the tetrahydrofuran ring [8].

A second distillation of the fraction with b.p. 78-90° (15-19 mm), obtained in the bisulfite treatment of 3-methylhexyne-1-diol-3,6 (III), yielded about 5 g (16%) of a substance which corresponded to the enyne alcohol (V) and became yellow on standing, even in sealed ampules.

B.p. 87-89° (19 mm), n_D^{20} 1.4833, d_4^{20} 0.9247, MR_D 33.99. $C_7H_{10}O$ ₣ ₣. Calculated 33.58. The constants agreed satisfactorily with literature data [5]; b.p. 72-74° (4 mm), n_D^{20} 1.4847, d_4^{20} 0.9174, MR_D 34.40.
Found %: OH 14.93. $C_7H_{10}O$. Calculated %: OH 15.44.

Attempts were made to isomerize the alcohol obtained into a tetrahydrofuran derivative.

1) When distilled with a drop of sulfuric acid at normal pressure, part of the alcohol was recovered (b.p. 150-155°, n_D^{20} 1.4840) and a considerable part of the alcohol polymerized.

2) When the enyne alcohol was treated with sodium bisulfite solution under the conditions used for dehydration of the glycol (III), about half of the alcohol was recovered (b.p. 155°, n_D^{20} 1.4821) and the rest formed a tar.

The 4th fraction, obtained in the bisulfite treatment of glycol (III), with b.p. 125-130° (15 mm), was the original glycol (n_D^{20} 1.4715); it formed a silver acetylide only on heating.

II. Dehydration of glycol (III) under the action of sulfuric acid. When the glycol was distilled with the vapor from aqueous 5 and 10% sulfuric acid, the sole product was 2,2-methylacetylenyltetrahydrofuran (IV) with b.p. 118-126°, n_D^{20} 1.4420, d_4^{20} 0.9120. The yield was 10%. The bulk of the substance polymerized.

When the vapor of the glycol was passed through a tube filled with pumice soaked in concentrated sulfuric acid at 100-125° (25 mm), a mixture of 2,2-methylacetylenyltetrahydrofuran and enyne alcohol was formed and these distilled-off with water. The reaction was accompanied by strong tar formation.

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*As in original – Publisher's note.

The best yield of 2,2-methylacetylenyltetrahydrofuran was obtained by distilling the glycol from a Wurtz flas, over pieces of pumice soaked in sulfuric acid, heated on Wood's alloy at 130-140° (40 – 35 mm). 40 g of glycol yielded 30 g of a crude mixture of the cyclic product and enyne alcohol. Distillation yielded 15 g (47%) of 2,2-methylacetylenyltetrahydrofuran.

B.p. 124-125°, n_D^{20} 1.4397, d_4^{20} 0.9118, MR_D 31.78. $C_7H_{10}OF$. Calculated 31.90.

The bulk of the enyne alcohol polymerized during distillation.

III. Unsuccessful attempts to prepare 2,2-methylacetylenyltetrahydrofuran. When the glycol (III) was distilled over $KHSO_4$ at 20 mm, the starting material distilled and part of the substance formed tar. When the glycol was distilled over oxalic acid (aqueous) at 115-120° (7 mm), the starting material was recovered.

9 g of the glycol was dissolved in 25 ml of wet ether, saturated with sulfur dioxide, the mixture again saturated with SO_2 and left overnight. After removal of the ether, the original glycol was distilled off and part of the substance formed tar.

When the glycol was distilled with the vapor from 0.4 and 1.6% sulfuric acid, the starting material was recovered.

Reaction of 2,2-methylacetylenyltetrahydrofuran with sodium and benzyl bromide in liquid ammonia. The reaction was performed in an open tube (6 cm diameter) with a capacity of 400-500 ml, fitted with a stirrer and placed in a Dewar vessel and cooled to – 40 to – 50° with a solution of carbon dioxide in ether. Into the tube was poured liquid ammonia (2/3 of the tube), followed by 15 g of 2,2-methylacetylenyltetrahydrofuran, and then 3 g of sodium was added in small pieces with stirring. The solution did not turn blue; the sodium disappeared rapidly and a portion of sodio derivative precipitated. After 30-40 minutes, 11 g of benzyl bromide, representing slightly less than the theoretical amount (12.4 g), was added. Stirring was continued until the precipitate of NaBr settled to the bottom. The mixture was left overnight, when the ammonia evaporated and next morning the reaction products were extracted with ether. The ether was removed and the residue vacuum-distilled. This gave the following fractions: 1st 33-38° (5-6 mm) in the receiver and 10 g of the starting material in a trap; 2nd 71-72° (4 mm), 4 g, n_D^{20} 1.5175, d_4^{20} 0.9537; 3rd 79° (4 mm), 2 g, n_D^{20} 1.5018.

The 2nd and 3rd fractions contained nitrogen, rapidly decolorized a solution of potassium permanganate and gradually crystallized as white plates with m.p. 98°.

The sodium derivative of 2,2-methylacetylenyltetrahydrofuran could not be obtained in xylene, even when the reaction mixture was boiled.

The sodium derivative of 2,2-methylacetylenyltetrahydrofuran was prepared in liquid ammonia as described above from 2.5 g of sodium and 12 g of 2,2-methylacetylenyltetrahydrofuran; after evaporation of the ammonia, the residual sodium derivative was boiled in anhydrous ether with 17 g of benzyl bromide for 4 hours. The following day, distillation of the reaction products gave an almost quantitative recovery of the starting materials.

Reaction of dimethylacetylenylcarbinol with sodium and ethyl bromide in liquid ammonia. 13 g of sodium was gradually added to 14 g of dimethylacetylenylcarbinol under the conditions described above for 2,2-methylacetylenyltetrahydrofuran. One hour after the beginning of the reaction, 19 g of ethyl bromide was added to the reaction mixture in small portions, avoiding vigorous boiling of the ammonia, and then stirring was continued for a further 1 hour. The following day, the reaction products were extracted with ether. After removal of the ether, the residue boiled at 89-91°. The yield was 7 g (37.5%). The substance gave a white precipitate with an ammonia solution of silver oxide and reacted with methylmagnesium iodide. Distillation on a column yielded 4 g of a substance which corresponded to the ethyl ether of dimethylacetylenylcarbinol (III).

B.p. 90-91°, n_D^{20} 1.4072, d_4^{20} 0.8035, MR_D 34.33. $C_7H_{12}OF$. Calculated 34.17.
Literature data [10]: b.p. 93°; n_D^{20} 1.4042, d_4^{20} 0.8125.
Found%: ethoxyl 40.50; number of active H atoms 0.56. $C_7H_{12}O$. Calculated %: ethoxyl 40.17; number of active H atoms 1.

Apparently the acetylenic hydrogen does not react with methylmagnesium iodide completely; dimethylacetylenylcarbinol and other acetylene alcohols react with only one molecule of methylmagnesium iodide due to the hydrogen of the hydroxyl group.

Reaction of dimethylacetylenylcarbinol with sodium and benzyl bromide in liquid ammonia. The reaction was performed under the conditions described above. 4.4 g of sodium was added to 16 g of dimethylacetylenylcarbinol. 30 g of benzyl bromide was added to the sodium derivative formed. After evaporation of the ammonia, the reaction products were extracted with ether, the ether distilled off and the residue distilled on a column to give the following fractions: 1st 51-61° (2 mm), 1.2 g, n_D^{20} 1.5306; 2 g 62-74° (2 mm), 1 g. (Both fractions contained traces of halogen and crystallized on the walls of the flask).

A 3rd fraction of 11 g (36%, calculated on the bromide taken) corresponded to the benzyl ether of dimethylacetylenylcarbinol (VII) and had the following constants.

B.p. 81-82° (2 mm), n_D^{20} 1.4990, d_4^{20} 0.9463, MR_D 53.95. $C_{12}H_{14}OF_3F$. Calculated 53.65. Found %: C 82.36; H 8.43; M 172. $C_{12}H_{14}O$. Calculated %: C 82.75; H 8.07, M 174.

For the substance with b.p. 81-82° (2 mm), we plotted the Raman spectrum on an ISP-51 apparatus with a slit of 0.005 and an exposure of 8-10 hours. The following data are the averages of three plots:

2108 (8); 1604 (5); 1452 (2); 1376 (1); 1207 (2); 1158 (1); 1026 (6); 1000 (10); 942 (4); 820 (1); 617 (2) cm^{-1}. The frequency of 2108 cm^{-1} is characteristic of a triple bond and the frequencies 1604, 1000, and 617 cm^{-1} correspond to the C_6H_5 group.

The infrared absorption spectra were plotted on an IKS-11 apparatus with an LiF prism, d 15 μ, and intense absorption at 3308 cm^{-1} was observed and this is characteristic of the valence oscillations of the $\equiv C-H$ group.

In other experiments on the reaction of dimethylacetylenylcarbinol with sodium and benzyl bromide, the yield of reaction product was ~ 40%; the product had b.p. 74.5-75° (1 mm), n_D^{20} 1.4995, d_4^{20} 0.9424.

Hydrogenation of benzyl ether of dimethylacetylenylcarbinol. 14 g of the substance with b.p. 74.5-75° (1 mm) was hydrogenated over 1.5 g of platinum black, when it absorbed 101% of the amount of hydrogen calculated for a triple bond. After removal of the alcohol, the residue was distilled to give 9 g of a substance corresponding to the benzyl ether of dimethylethylcarbinol.

B.p. 118.5°, n_D^{20} 1.4853, d_4^{20} 0.9175 [11], MR_D 55.72. $C_{12}H_{18}OF_3$. Calculated 55.66. Found %: C 80.85; H 10.31. $C_{12}H_{18}O$. Calculated %: C 80.99; H 10.11.

Ozonization of benzyl ether of dimethylacetylenylcarbinol. 3 g of substance absorbed 1.11 g of ozone, which represents 130% of theoretical. When the ozonide had been decomposed with water, part of the solution was used for a formic acid determination by Fincke's method [12] (72%). Formaldehyde was not detected by a dimedone test. The neutral ozonolysis products were steam-distilled from the rest of the solution into a solution of 2,4-dinitrophenylhydrazine. The 2,4-dinitrophenylhydrazone obtained was difficultly soluble in alcohol and slightly more so in ethyl acetate. After several recrystallizations from the latter, it was separated into two products. The difficultly soluble product had m.p. 235° and did not depress the melting point of authentic benzaldehyde 2,4-dinitrophenylhydrazone (m.p. 234°) [13]. The 2,4-dinitrophenylhydrazone, which was readily soluble in alcohol and ethyl acetate, had m.p. 122°, after three recrystallizations from alcohol.

Found %: N 22.32. Calculated for methacrolein 2,4-dinitrophenylhydrazone $C_{10}H_{10}O_4N_4$ %: N 22.40.

The neutral solution of ozonolysis products was acidified with dilute sulfuric acid and the formic acid distilled-off. The solution of nonvolatile acids was neutralized with sodium carbonate, evaporated down, again acidified with sulfuric acid and then extracted with ether. After removal of the ether, the residue was placed in a vacuum desiccator over K_2CO_3 to remove the excess formic acid. As a result, we obtained 0.9 g of benzyloxyisobutyric acid as a brownish oil.

Found: equiv. 181.5. $C_{11}H_{14}O_3$. Calculated: equiv. 194.

0.82 g of the acid was dissolved in ammonia and after removal of the excess ammonia, the solution was treated with silver nitrate solution.

Found %: C 44.30; H 3.90; Ag 37.71. $C_{11}H_{13}O_3Ag$. Calculated %: C 43.85; H 4.32; Ag 36.21.

SUMMARY

1. It was shown that the dehydration of 3-methylhexyne-1-diol-3,6 proceeds in two directions to form 2,2-methylacetylenyltetrahydrofuran and an enyne alcohol – 3-methylhexen-3-yn-1-ol-6, which is largely polymerized under the reaction conditions.

2. It was shown that the enyne alcohol is not isomerized into 2,2-methyl acetylenyltetrahydrofuran.

3. It was shown that treatment of 2,2-methylacetylenyltetrahydrofuran with sodium produced deep changes in the structure of the tetrahydrofuran derivative, which made it impossible to prepare 2,2-methylbenzylacetylenyltetrahydrofuran, starting from 2,2-methylacetylenyltetrahydrofuran.

4. It was established that treatment of dimethylacetylenylcarbinol with sodium and halogen derivatives – ethyl bromide and benzyl bromide – in liquid ammonia yielded the corresponding ethers of dimethylacetylenylcarbinol.

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*Original Russian pagination. See C.B. Translation.

**Names not verified – Translator's note.

HOMOLOGS OF MONOVINYLACETYLENE

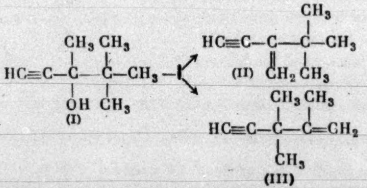
VIII. SPECTRAL CHARACTERISTICS OF AN ENYNE HYDROCARBON — 3',3'-METHO-3-ETHYLBUTEN-3-YNE-1 — AND ITS DERIVATIVES

Iu. P. Artsybasheva and I. A. Favorskaia

The present report is devoted to a spectral investigation of some unsaturated compounds with a tert-butyl group.

The inertness of 3,4,4-trimethylpentyn-1-ol-3 (I) in the substitution of the hydroxyl by halogen was noted previously [1] and the dehydration of this carbinol was studied. The structure of the hydrocarbon obtained in the dehydration was proved by oxidation with permanganate. Trimethylpyruvic acid was identified among the oxidation products as its p-nitrophenylhydrazone and on the basis of these data, the hydrocarbon was assigned the structure of 3',3'-metho-3-ethylbuten-3-yne-1 (II). However, since oxidation with permanganate is not as yet a quantitative method, we cannot exclude the possibility that the investigated hydrocarbon contained some of the isomeric hydrocarbon with unconjugated bonds — 3,4,4-trimethylpenten-4-yne-1 (III); this could also explain the anomalously low exaltation of the molecular refraction and the relative dispersion of the hydrocarbon.

We were interested in the problem of the spectral proof of the structure of the products obtained by the dehydration of carbinol (I), from the point of view of a possible rearrangement with a change in the carbon skelton, characteristic of saturated alcohols with a neopentyl grouping [2].

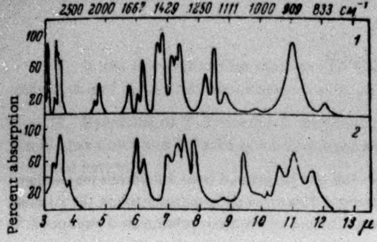


(I) (II) (III)

The carbinol (I) was dehydrated over anhydrous magnesium sulfate at 280-300°. The infrared absorption spectra of the products obtained were plotted. The spectrum (figure) showed bands indicating that the hydrocarbon obtained was the individual product (II) of a normal dehydration of the carbinol (I). The band at 1606 cm^{-1} belonged to valence oscillations of the conjugated double bond [3] and the presence of a band at 2099 cm^{-1} indicated the presence of a conjugated monosubstituted acetylene bond. A similar shift in the absorption bands from their normal position in the presence of conjugation in an enyne system, has been noted in the literature many times [4-8]. Bands indicating the presence of isolated double and triple bonds were not observed.

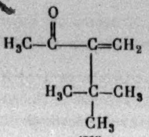
This makes the absence of exaltation of the molecular refraction and the low relative dispersion (ω_{FCD} 25.33) of the hydrocarbon [9] all the more interesting. This discrepancy may be explained by disruption of the coplanarity of the system due to steric hindrance caused by the tert-butyl radical. However, this postulate can only be confirmed by calculation and the construction of appropriate models, as will be done in the next report.

Interesting data were obtained in the spectral investigation of the hydration products of the hydrocarbon obtained. With a mixture of the hydrocarbons (II and III) present in the dehydration product of the carbinol (I), the

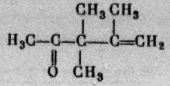


Infrared spectra. 1) 3',3'-metho-3-ethylbuten-3-yne-1 (II); 2) 3',3'-metho-3-ethylbuten-3-one-2 (IV).

hydration should give a mixture of conjugated – 3',3'-metho-3-ethylbuten-3-one-2 (IV) – and unconjugated – 3,4,4-trimethylpenten-4-one-2 ketones.



(IV)



(V)

The infrared and ultraviolet absorption spectra of the hydration products were plotted. The infrared spectrum showed a band caused by the presence of a conjugated carbonyl (1689 cm^{-1}) and a double bond (1610 cm^{-1}) [3]. It is very difficult to indicate the exact position of the absorption band of the double bond, due to the intense absorption of the carbonyl and the partial superposition of these bands. Intense absorption at 1361 and 1385 cm^{-1} [3] indicated the presence of a tert-butyl radical in the ketone. The absorption of the ketone in the ultraviolet region was characterized by the presence of two maxima at λ_{max} 220 mμ (ϵ_{max} ~ 17000) and λ_{max} 304 mμ (ϵ 21).

According to literature data [10], α, β-unsaturated ketones have a strong ultraviolet band at λ ~ 235 mμ (ε ~ 12000) and a weak band at λ 320 mμ (ε ~ 40).

The presence of an intense band in the range 220-250 mμ in the spectrum of the carbonyl compound may be considered as proof of the conjugation of the ethylene and carbonyl groups; the long-wave band may be considered as a displaced carbonyl band. Consequently, on the basis of infrared and ultraviolet absorption spectral data, we may consider that the ketone corresponds to formula (IV) and is the hydration product of hydrocarbon (II).

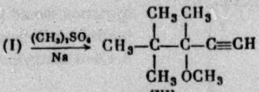
It is reported in the literature [11] that in going to ketone derivatives, there is an increase in the main absorption maximum and it is shifted towards longer wavelengths. Therefore, absorption spectra of derivatives are often used in the identification of carbonyl compounds.

It is known that semicarbazones of saturated ketones in alcohol have an intense band at λ 228-230 mμ (ε ~ 10000-13000), and the band typical of semicarbazones of α, β-unsaturated ketones appears in the range 260-273 mμ (ε ~ 20000) (12). A series of works has been devoted to the study of the absorption spectra of 2,4-dinitrophenylhydrazones [13].

We prepared derivatives of ketone (IV) and plotted their spectra. The spectrum of the semicarbazone had an absorption band at 233 mμ (ε 10000), and the spectrum of the 2,4-dinitrophenylhydrazone of ketone (IV) in isooctane had a weak band at 408 mμ and an intense band at 348 mμ (ε 17000). The data obtained indicate that the semicarbazone and the 2,4-dinitrophenylhydrazone of ketone (IV) have ultraviolet absorptions typical of derivatives of unconjugated ketones, while ketone (IV) itself absorbs like an α,β-unsaturated ketone.

Similar cases are also noted in the literature [14] for some cyclohexane derivatives. The semicarbazone of the α,β-unsaturated ketone, 2-n-butyl-1-acetylcyclohexene-1, has an absorption maximum at 226 mμ (ε 12000), which agrees with the absorption maximum of the semicarbazone of the saturated ketone, 2-methyl-1-acetylcyclohexane (λ 225 mμ, ε 12300). Evidently, in this case the absorption and intensity of the absorption band in the electron spectra depend on the character of the substituent, causing disruption of the coplanarity of the system. The absorption of nonplanar system is characterized by a fall in intensity and a hypsochromic effect.

It seemed interesting to us to methylate carbinol (I) to determine the effect of the tert-butyl radical on the possibility of substituting the hydrogen of the hydroxyl group and the substitution capacity of the free acetylenic hydrogen. The reaction gave the ether, 3,4,4-trimethyl-3-methoxypentyne-1 (VI) in 50% yield, calculated on the carbinol which reacted. Not even traces of an alcohol with a longer chain were found in the methylation products.



$$\text{(I)} \xrightarrow[\text{Na}]{(CH_3)_2SO_4} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{\overset{CH_3}{|}}{\underset{\underset{OCH_3}{|}}{C}}-C\equiv CH$$

(VI)

EXPERIMENTAL

Dehydration of 3,4,4-trimethylpentyn-1-ol-3 (I). The reaction was performed over anhydrous magnesium sulfate in a stream of nitrogen at 280-300°. The yield of hydrocarbon (II) was ~ 65%, calculated on the carbinol reacted. The hydrocarbon 3',3'-metho-3-ethylbuten-3-yne-1 was distilled twice on a column in a stream of nitrogen.

B.p. 47° (130 mm), n_D^{20} 1.43147, n_C^{20} 1.42841, n_F^{20} 1.43934, ω_{FCD}25.33, d_4^{20} 0.7609, MR_D 36.74. C_8H_{12}F F. Calculated 36.67. EMR_D + 0.07.

The hydrocarbon give a precipitate with an ammonia solution of silver oxide.

Spectrum of hydrocarbon plotted in the region 3-12μ on an IKS-11 apparatus with NaCl and LiF prisms in a 50μ layer. Found (in cm^{-1}): 830 w; 903 s; 1121 w; 1161 av; 1199 av; 1361 s; 1385 av; 1395 av; 1456 vs; 1478 s; 1606 av; 1681 w; 2099 av; 2154 w; 2863 s; 2904 s; 2958 vs; 3094 w; 3301 vs.

Hydration of hydrocarbon (II). Preparation of 3',3'-metho-3-ethylbuten-3-one-2 (IV). Into a three-necked flask, fitted with a stirrer, a reflux condenser and a thermometer, was placed 10 g of hydrocarbon (II), 2.4 g of mercuric oxide, 7 ml of concentrated sulfuric acid, 20 ml of a 50% solution of ferric sulfate and 170 ml of water. The reaction mixture was stirred vigorously and heated at 80° for 3 hours. The ketone was steam-distilled and extracted with ether. The ether extracts were dried with calcium chloride. The ketone was vacuum-distilled on a column.

B.p. 73-74° (96 mm), n_D^{20} 1.43465, n_C^{20} 1.43182, n_F^{20} 1.44171, ω_{FCD} 22.75; d_4^{20} 0.8513, MR_D 38.58. $C_8H_{14}O$F. Calculated 38.69.
Found %: C 75.96; H 11.43. $C_8H_{14}O$. Calculated %: C 76.13; H 11.18.

The infrared spectrum of the ketone was plotted on an IKS-11 apparatus with a layer thickness of 10μ and NaCl and LiF prisms.

Found (in cm^{-1}): 855 av; 904 s; 942 av; 984 w; 1071 av; 1280 s; 1345 vs; 1365 s; 1385 av; 1442 av; 1610 av; 1689 s; 2868 vs; 3075 s.

The ultraviolet spectrum was plotted on an SF-4 apparatus. Found: λ_{max} 220 mμ, ϵ_{max} 17000; λ'_{max} 304 mμ, ϵ'_{max} 21 (in alcohol).

Semicarbazone of ketone (IV). The m.p. was 164-166° (alcohol).

Found %: C 59.43; H 9.33; N 22.63. $C_9H_{17}ON_3$. Calculated %: C 59.43; H 9.28; N 22.40.

Ultraviolet spectrum: λ_{max} 233 mμ, ϵ_{max} 10900 (in alcohol).

2,4-Dinitrophenylhydrazone of ketone (IV). The m.p. was 109-111° (alcohol).

Found %: C 54.64; H 6.18; N 18.19. $C_{14}H_8O_4N_4$. Calculated %: C 54.89; H 5.92; N 18.28.

Ultraviolet spectrum: λ_{max} 348 mμ, ϵ_{max} 16800 (in isooctane).

Methylation of carbinol (I). Into a wide tube, placed in a Dewar flask and cooled with carbon dioxide, was poured 250 ml of liquid ammonia. The reaction was performed at − 34°. With stirring, 15 g of carbinol and 5.5 g of sodium in small pieces were introduced into the tube. When all the sodium had been added, the mixture was stirred for a further 20-30 minutes. Then dimethyl sulfate (15 g) was added over a period of 2 hours with vigorous stirring. When the ammonia had evaporated completely, water was added to the tube until the residue dissolved. The reaction products were extracted with ether. The ether extracts were washed with 2% acetic acid and water and dried over potassium carbonate. The product obtained was vacuum-distilled on a column. The 3,4,4-trimethyl-3-methoxypentyne-1 (VI) had the following constants:

B.p. 72-74° (95 mm), n_D^{20} 1.4294, d_4^{20} 0.8380. MR_D 43.62. $C_9H_{16}O$F. Calculated 43.40. EMR_D + 0.22.
Found %: C 77.30; H 12.02; OCH_3 20.98. $C_9H_{16}O$. Calculated %: C 77.09; H 11.62; OCH_3 21.10.

SUMMARY

1. It was established that there was no rearrangement with a change in the carbon skeleton during the dehydration of 3,4,4-trimethylpentyn-1-ol-3.

2. Hydration of 3',3'-metho-3-ethylbuten-3-yne-1 yielded the ketone 3',3'-metho-3-eth lbuten-3-one-2, whose ultraviolet and infrared spectral characteristics corresponded to the characteristics of a conjugated α,β-unsaturated ketone.

3. It was shown that the semicarbazone and 2,4-dinitrophenylhydrazone of the α,β- unsaturated ketone, 3',3'-metho-3-ethylbuten-3-one-2 absorbed in the ultraviolet region like derivatives of saturated ketones.

4. 3,4,4-Trimethylpentyn-1-ol-3 was methylated. The ether, 3,4,4-trimethyl-3-methoxypentyne-1 was obtained.

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*Original Russian pagination. See C.B. Translation.

**In Russian.

THE CYANOETHYLATION OF ACETYLENE γ-GLYCOLS

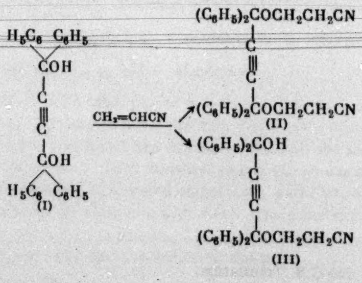
A. I. Zakharova and A. M. Efros

The addition of acrylonitrile to acetylene γ-glycols was first studied by Nazarov and Shvekhgeimer [1]. They cyanoethylated the simplest diprimary acetylene glycol – butynediol-1,4 – and the ditertiary acetylene glycol – tetramethylbutynediol – in the presence of a 40% aqueous solution of potassium hydroxide. The former smoothly added two molecules of acrylonitrile in dioxane solution to form the di(β-cyanoethyl) ether. Cyanoethylation of tetramethylbutynediol in this solvent required heating of the reaction mixture at 60-75° for 6 hours and this gave a mixture of the mono- and di-(β-cyanoethyl) ethers in approximately equal amounts.

Recently, one of us studied [2] the cyanoethylation in the benzimidazole series in the presence of triethylbenzylammonium hydroxide. It seemed interesting to test the possibility of using this catalyst in the cyanoethylation of unsaturated, hydroxy-containing compounds, in particular, acetylene γ-glycols. With this aim, we cyanoethylated two acetylene γ-glycols – tetramethyl- and tetraphenylbutynediols – in the presence of triethylbenzylammonium hydroxide. The cyanoethylation of tetramethylbutynediol in the presence of this catalyst proceeded very readily when a dioxane solution of the glycol was treated with a twofold excess of acrylonitrile and was accompanied by the evolution of a little heat and very slight tar formation. The reaction mixture was kept at room temperature for 24 hours and poured into water to deposit crystals of the di(β-cyanoethyl) ether of tetramethylbutynediol; after recrystallization from petroleum ether, the substance had m.p. 37-38°. The yield was 65%.* Under these conditions, the monocyanoethyl ether of the glycol is formed in a yield of not more than 8-10%.

Thus, it was found that triethylbenzylammonium hydroxide could be used successfully in the cyanoethylation of tetramethylbutynediol; the process proceeds under milder conditions than in the presence of 40% potassium hydroxide solution and the main reaction product – the di(β-cyanoethyl) ether of the glycol – precipitates immediately in the crystalline state and does not require long purification.

The cyanoethylation of tetraphenylbutynediol (I) in the presence of triethylbenzylammonium hydroxide also proceeded readily at room temperature as a result of the reaction of a dioxane solution of the glycol with a 2.5-fold excess of acrylonitrile. After standing for 48 hours, the reaction mixture deposited crystals which had m.p. 179-180° after recrystallization, and were the di-(β-cyanoethyl) ether of tetraphenylbutynediol (II). The yield was 52.6%. Working up the residual reaction mixture appropriately yielded the mono-β-cyanoethyl ether of the glycol (III) with m.p. 68-69°. The yield was 26.5%. Neither of the ethers are described in the literature.



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* According to the data in [1], the di(β-cyanoethyl) ether of tetramethylbutynediol, after 5 distillations in vacuum, is a colorless, thick liquid, which crystallizes on standing; the m.p. is about 25°.

EXPERIMENTAL

Cyanoethylation of tetramethylbutynediol. Into a flask was placed 7 g of tetramethylbutynediol, 0.7 g of triethylbenzylammonium hydroxide and 10 ml of dioxane. 16.4 ml of acrylonitrile (twofold excess) was gradually added from a dropping funnel over a period of 30 minutes, when very slight tar formation was observed and the reaction mixture evolved heat. After 24 hours, the reaction mixture was poured into water and an oily layer was formed on the bottom of the flask, which crystallized when rubbed with a glass rod. The crystals were separated from the small amount of oily liquid and recrystallized, first from water and then from petroleum ether, when they melted at 37-38° and analyzed as the di(β-cyanoethyl) ether of tetramethylbutynediol. The yield was 8 g (65%).

Found %: C 67.98, 68.03; H 7.72, 8.03; N 11.52, 11.38. M 250. $C_{14}H_{20}O_2N_2$. Calculated %: C 67.74; H8.07; N 11.29. M 248.

When distilled in vacuum, the uncrystallizable fraction, collected from several experiments, had b.p. 112-113° at 3 mm and was the mono-β-cyanoethyl ether of tetramethylbutynediol according to its constants [1].

Cyanoethylation of tetraphenylbutynediol. Into a two-necked flask, fitted with a reflux condenser and a dropping funnel, was placed 15 ml of dry dioxane, 15 g of tetraphenylbutynediol and 1 g of triethylbenzylammonium hydroxide. 10 g of acrylonitrile was gradually added at room temperature from the dropping funnel over a period of 15 minutes; slight tar formation was observed in the reaction mixture, but no noticeable heat evolution. After 48 hours, coarse crystals were deposited on the bottom of the flask and these were separated from the mother solution. After two recrystallizations from acetone and then from alcohol, the substance had m.p. 179-180°. A mixture with the original glycol (m.p. 199°) melted at 159-162°. The yield of the di-(β-cyanoethyl) ether of tetraphenylbutynediol (II) was 10 g (52.6%).

Found %: C 82.54, 82.39; H 5.87, 5.74; N 5.69, 5.89. M 490. $C_{34}H_{28}O_2N_2$. Calculated %: C 82.23; H 5.67; N 5.62. M 496.

20 ml of water was added to the mother liquors left after separation of the crystals of the di-(β-cyanoethyl) ether of the glycol. A crystalline product precipitated and this was filtered off and recrystallized twice from petroleum ether. We obtained white, lustrous crystals of the mono-β-cyanoethyl ether of tetraphenylbutynediol (III) with m.p. 68-69°. The yield was 3 g (26.5%). The ether was readily soluble in alcohol.

Found %: C 83.99, 84.30; H 5.36, 5.43; N 3.11, 3.14. M 240. $C_{31}H_{25}O_2N$. Calculated %: C 83.92; H 5.63; N 3.15. M 248.

SUMMARY

1. The γ-acetylene glycols, tetramethyl- and tetraphenylbutynediol, were cyanoethylated with acrylonitrile in the presence of triethylbenzylammonium hydroxide.

2. It was shown that cyanoethylation in the presence of this catalyst proceeds under mild conditions without heating and that the reaction products are obtained in good yields.

3. The mono- and di-(β-cyanoethyl) ethers of tetraphenylbutynediol were prepared and characterized for the first time.

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*Original Russian pagination. See C.B. Translation.

THE REACTION OF NITROSYL CHLORIDE WITH UNSATURATED HYDROCARBONS

IV. THE REACTION WITH BUTENE-1

K. A. Ogloblin

In a previous communication [1] it was pointed out that the reaction of nitrosyl chloride with hydrocarbons containing an ethylene bond has mainly been investigated with tri- and completely substituted ethylene hydrocarbons, hydrocarbons of the cyclohexene series and in the terpene series [2], where it is often used to determine the degree of substitution of the carbon atoms at the double bond, but that it has hardly been investigated with mono- and disubstituted ethylenes.

It was previously established that in the reaction of nitrosyl chloride with 2-methylbutene-3 [1], the main products were 4-nitro-3-chloro-2-methylbutane and 3,4-dichloro-2-methylbutanes, i.e., the primary reaction product, 4-nitroso-3-chloro-2-methylbutane, is oxidized by the nitrosyl chloride to the nitro compound and the chlorine liberated in the decomposition of the nitrosyl chloride gives the dichloride with the hydrocarbon. To determine how typical this reaction course was for other monosubstituted ethylene hydrocarbons, an investigation was made of the reaction of nitrosyl chloride with butene-1. The reaction was performed in ether solution, in sealed ampules at room temperature. As in the case of isopropyl ethylene, considerable pressure was generated in the ampules and this often burst the ampules. To decrease the possibility of bursting the ampule, the reaction was performed with less concentrated reagent solutions and only one third of the volume of the ampule was filled with the reaction mixture.

Butene-1 was more inert in the reaction with nitrosyl chloride than 2-methylbutene-3, which may be explained, on one hand, by the lower polarization of the double bond in butene-1 in comparison with 2-methylbutene-3 and also by the fact that the reaction with butene was performed with less-concentrated solutions.

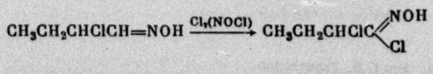
As in the case of isopropyl ethylene, the main reaction products from butene-1 and nitrosyl chloride were the nitrochloro compound, 1-nitro-2-chlorobutane, and the dichloride, 1,2-dichlorobutane. The 1-nitroso-2-chlorobutane, formed in the first stage, was oxidized by the nitrosyl chloride to 1-nitro-2-chlorobutane and the chlorine, formed by decomposition of the nitrosyl chloride, gave the dichloride with the hydrocarbon.

$$CH_3CH_2CH{=}CH_2 \xrightarrow{NOCl} CH_3CH_2CHClCH_2NO$$

$$CH_3CH_2CHClCH_2NO \xrightarrow{NOCl} CH_3CH_2CHClCH_2NO_2 + N_2 + Cl_2$$

$$CH_3CH_2CH{=}CH_2 \xrightarrow{Cl_2} CH_3CH_2CHClCH_2Cl$$

The absence of the oxime of α-chlorobutyraldehyde from the reaction products indicated the very low rate of the rearrangement of the nitroso compound in comparison with the oxidation reaction. The presence of α-chlorobutyrohydroxyamyl chloride in the reaction products, indicated the formation of the chloro oxime, since the former was apparently produced by the action of chlorine or nitrosyl chloride on the oxime [3].



$$CH_3CH_2CHClCH{=}NOH \xrightarrow{Cl_2(NOCl)} CH_3CH_2CHClC\begin{matrix}\diagup NOH \\ \diagdown Cl\end{matrix}$$

The structure of 1-nitro-2-chlorobutane was proved by converting it into α-chlorobutyric acid by heating it in sealed ampules at 140-145° [1].

$$CH_3CH_2CHClCH_2NO_2 \xrightarrow{HCl,\ H_2O} CH_3CH_2CHClCOOH + NH_2OH \cdot HCl$$

Thus, as with 2-methylbutene-3, the reaction of nitrosyl chloride with butene-1 gives mainly the nitrochloro compound and the dichloride.

EXPERIMENTAL

Butene-1 was synthesized from allyl bromide and methylmagnesium iodide [4] and was used for the reaction without additional purification.

Nitrosyl chloride was prepared by reacting sodium nitrite with hydrochloric acid (d 1.19) [9]. To remove hydrogen chloride and oxides of nitrogen, the product was boiled for 30-40 minutes under reflux (minus 30-40°) and then distilled.

Reaction of nitrosyl chloride with butene-1. 98 g of nitrosyl chloride (− 50°) was added with stirring to a solution of 51 g of butene-1 in 500 ml of anhydrous ether, cooled to − 12°. The brown-red solution was poured into 19 ampules, cooled to − 17°; the ampules were sealed and placed in water at + 3°. The next day, the temperature of the bath was + 16° and the ampules contained a brown-orange liquid without any red tinge. The next day the color of the reaction mixture was brownish green and on the third day, the homogeneous solution was slightly paler than on the day before. The ampules were cooled (− 50°) and opened[*] by heating the ends with the flame of a torch, when high pressure was found to have been generated. The reaction mixture was washed three times with water, when the unreacted nitrosyl chloride was hydrolyzed to liberate brown vapors of nitrogen oxides, and the wash water was found to contain 12.1 g of hydrogen chloride.[**] The green ether solution was washed with 5% sodium carbonate solution (5 × 100 ml) and then twice with water. After being dried with anhydrous sodium sulfate, the ether solution had a light-green color. The volatile products were distilled in vacuum and caught in traps (− 50°). The residue was vacuum-distilled. By subsequent distillations, the volatile products and residue were separated into fractions: 1st b.p. 41.5-42° at 40 mm, weight 13.6 g; 2nd b.p. 54-56° at 40 mm, 1.75 g; 3rd b.p. 56.5° at 4 mm, 18.0 g; 4th b.p. 77-78° at 4 mm, 2.3 g.

Investigation of fractions. 1st Fraction − a colorless, clear, mobile liquid.

d_4^{20} 1.1161, n_D^{20} 1.4445, MR_D 30.26; calc. 30.40.
Found %: Cl 53.29, 53.65. $C_4H_8Cl_2$. Calculated %: Cl 55.8.

The substance was 1,2-dichlorobutane (According to data in [5]: b.p. 123-125° at 758 mm, d_4^{20} 1.1187, n_D^{20} 1.440).

The 2nd fraction was a colorless mobile liquid with a pleasant smell, d_4^{20} 1.0520, n_D^{20} 1.4320. It was insoluble in water. It slowly decolorized a solution of potassium permanganate in acetone and did not reduce Fehling's solution. It gave qualitative reactions for nitrogen and chlorine (fusion with metallic sodium) and a nitrogen content of 2.6 and 2.3% (Dumas microdetermination). The substance was not identified.

The 3rd fraction was a colorless, clear liquid with a specific smell, insoluble in water and stable during storage.

d_4^{20} 1.2032, n_D^{20} 1.4510, MR_D 30.79;
Found %: N 9.76, 10.06; Cl 25.98, 26.03. $C_4H_8O_2NCl$. Calculated %: N 10.18; Cl 25.77.

The fraction was 1-nitro-2-chlorobutane (according to data in [6]: b.p. 78° at 13 mm, d_4^{20} 1.194, n_D^{20} 1.4480).

The 4th fraction was a clear, viscous liquid with d_4^{20} 1.3017, n_D^{20} 1.4864. It rapidly decomposed to form hydrogen chloride and colorless crystals (hydroxylamine hydrochloride). It was hydrolyzed by water, slowly in the cold and rapidly when heated. The aqueous solution had an acid reaction and gave a precipitate of silver chloride with silver nitrate solution and a reaction for hydroxamic acid with ferric chloride solution (red-violet color).

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[*] One of the ampules was not opened for several more days, but no further noticeable changes in the color occurred.

[**] Before titration of the wash water, the nitrous acid was destroyed by the addition of thiourea.

The 4th fraction was α-chlorobutyrohydroxamyl chloride.

Conversion of 1-nitro-2-chlorobutane into α-chloro-n-butyric acid. To prove the structure of the nitrochlorobutane, an investigation was made of the conversion of primary nitrohydrocarbons into carboxylic acids [7]. 5.3 g of 1-nitro-2-chlorobutane (b.p. 56.6° at 4 mm) and 10 ml of hydrochloric acid (d 1.19) were heated in a sealed ampule at 140-145° for 6 hours. The next day, colorless crystals appeared in the ampule in addition to the oily and the aqueous layer. The ampule was opened and contained a slight pressure. The contents of the ampule were diluted with water (the crystals dissolved completely) and the aqueous solution was treated with ether (6 x 20 ml); the oil passed into the ether solution, the latter was dried with sodium sulfate, the ether removed and the residue vacuum-distilled. Fractions of α-chloro-n-butyric acid were obtained: 1st, b.p. 68-72° at 4mm, 0.93 g, n_D^{20} 1.4453; 2nd, b.p. 72-74° at 4 mm, 2.2 g, d_4^{20} 1.1971, n_D^{20} 1.4407, MR_D 27.01; calc.27.07 (according to data in [8]: b.p. 101.25° at 15 mm, d_4^{20} 1.1796, n_D^{20} 1.4411).

Found: Neutralization equiv. 129.8. $C_4H_7O_2Cl$. Calculated: Neutralization equiv. 122.6.

The aqueous solution was evaporated to dryness. We obtained 1.72 g of hydroxylamine hydrochloride.

SUMMARY

1. The reaction of nitrosyl chloride with butene-1 in ether solution gave, as the main products, 1-nitro-2-chlorobutane and 1,2-dichlorobutane and a small amount of α-chlorobutyrohydroxamyl chloride.

2. The initial product – a chloronitroso compound – was oxidized to 1-nitro-2-chlorobutane and the chlorine, formed by decomposition of nitrosyl chloride, gave 1,2-dichlorobutane with butene.

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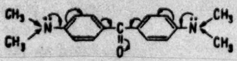
INVESTIGATION IN THE FIELD OF COMPOUNDS CONTAINING A THREE-MEMBERED OXIDE RING

XXIV. SYNTHESIS OF β,β'-DISUBSTITUTED NITRILES OF GLYCIDIC ACIDS

B. F. Martynov and A. V. Shchelkunov

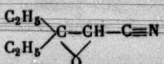
In a previous report [1], we described the reaction of monochloroacetonitrile with some ketones, which gave β,β'-disubstituted nitrile of glycidic acids, not described in the literature. To investigate the possibilities of synthesizing this class of compound, we reacted monochloroacetonitrile with a further series of ketones of aliphatic, aliphatic-aromatic and aromatic character, namely, diethyl, diisobutyl, dibenzyl, diphenyl, di-p-tolyl and di-p-dimethylaminophenyl ketones.

Of all the ketones listed here which underwent the condensation reaction, diisobutyl ketones gave the worst yield of final product. This is evidently explained by steric hindrance caused by the presence of the two isopropyl groups, which impede the approach of reagents to the carbonyl group. We should note that the reaction of this ketone (under the normal conditions) with ethyl monochloroacetate did not lead to the formation of a glycidic ester. As regards the other ketones, the highest yields of nitriles of glycidic acids were given by the aromatic ketones, diphenyl (81%) and di-p-tolyl ketones (80%). Michler's ketone did not condense with monochloroacetonitrile, despite many attempts to perform the reaction with freshly vacuum-distilled ketone. This can hardly be explained by steric hindrance, since the dimethylamino group is in a position para to the carbonyl. A more likely explanation may be found in peculiarities in the electronic structure of this ketone. It is known that the dimethylamino group possesses a very strongly expressed + I-effect, which may be readily transmitted through the benzene ring in a ketone with this structure and decrease the electrophilic properties of the carbonyl carbon atom.



Since there are two such groups here, their total effect may be so strong that the carbonyl group is practically incapable of adding nucleophilic reagents.

As a result of our work, we obtained the following five nitriles of glycidic acid.



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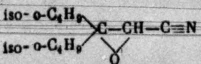

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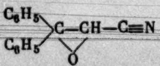

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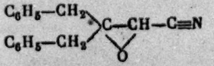

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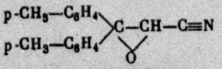


(V)

Of these, the nitrile of diphenylglycidic acid is known [2], but the rest are not described in the literature.

An examination of the properties of the nitriles listed showed the great stability of the nitriles containing aromatic substituents. The other nitriles darkened in time and formed a brown precipitate. The more stable

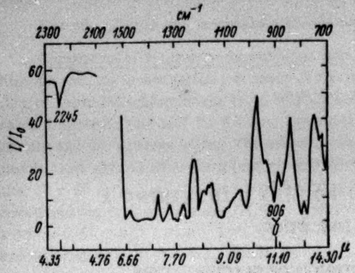


Fig. 1. Transmission spectrum of the nitrile of β,β'-dimethylglycidic acid (plotted with a thin layer with α 0.004 cm).

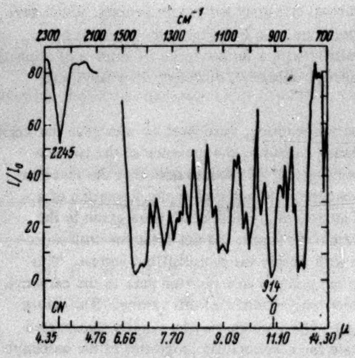


Fig. 2. Transmission spectra of the nitrile of β-pentamethyleneglycidic acid (plotted with a thin layer with α 0.006 cm).

nitriles could be vacuum-distilled. The nitriles of glycidic acids containing aliphatic radicals were almost impossible to obtain in a pure form – they always contained halogen. The traces of halogen may be explained by side reactions forming the α-chloronitrile of the corresponding unsaturated acid [3].

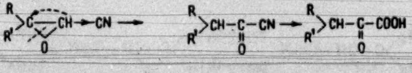
We plotted the Raman spectra of β,β'-dimethylglycidonitrile and confirmed this postulate: a weak band at the characteristic absorption frequency of a double bond (1662 cm^{-1}) was observed. In addition to the weak double bond line, the spectrum showed a very intense nitrile line (2245 cm^{-1}); guided by previous work [4], we assigned the line at 909 cm^{-1} to the oxide ring of β,β'-dimethylglycidonitrile. Together with this, a Beilstein test showed the presence of chlorine in a series of simple glycidonitriles. Carbon analyses, carried out after careful, repeated distillations of the β,β'-dimethyl- and β,β'-diethylglycidonitriles, gave low carbon percents and indicated the approximate content of the corresponding chlorocyanoethylene. Similar mixtures contained about 97% of glycidonitrile.

Having a spectrum of the mixture, it seemed interesting to obtain a Raman spectrum of a pure glycidonitrile. The most convenient material for this purpose was β-pentamethyleneglycidonitrile [1]. Its spectrum showed a very intense nitrile group line (2245 cm^{-1}), the frequency of the cyclohexane ring (708 cm^{-1}) and the frequency of an oxide ring (914 cm^{-1}).

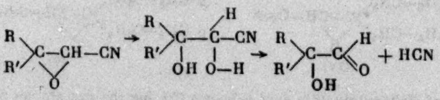
Besides the Raman spectra of the glycidonitriles, we also plotted their infrared spectra (Figs. 1 and 2); the latter confirmed the previous results. The infrared spectra were plotted on an IKS-11* with an NaCl prism.

To prove the structure of the glycidonitriles obtained, β-pentamethyleneglycidonitrile was hydrolyzed with acid. One would expect the following three directions for the hydrolysis of these compounds in the presence of concentrated sulfuric acid.

A. An initial isomerization of the starting glycidonitrile into the nitrile of an α-ketoxyacid; on hydrolysis the latter would give a disubstituted pyruvic acid.



B. Opening of the oxide ring to form the nitrile of an α,β-dihydroxycarboxylic acid, which then may be cleaved to an α-hydroxyaldehyde and hydrogen cyanide under the conditions of the acid hydrolysis [5].



C. Saponification of the nitrile group of the glycidonitrile with subsequent formation of a glycidic acid, which is decarboxylated and the oxide ring opened to give the corresponding aldehyde.

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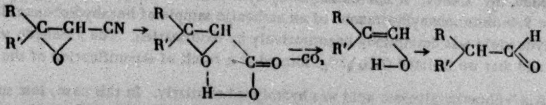

These conversions of glycidic acids in an acidic medium into the corresponding aldehydes have been described and are widely used nowadays as a method of preparing the latter [6]. The investigation performed showed that the acid hydrolysis proceeded mainly by mode C.

EXPERIMENTAL

The nitrile of β,β'-diethylglycidic acid (I). Into a three-necked, round-bottomed flask with a mercury seal and a stirrer was placed 10 ml of chloroacetonitrile and 13 ml of diethyl ketone (in this and subsequent syntheses, the starting materials were distilled immediately before the reaction; all the syntheses were performed in one day). Then approximately 100 ml of absolute ether was added and the flask with the reaction mixture cooled in ice and salt. When the temperature of the reaction mixture reached − 10°, 13 g of dry sodium ethylate was added to it in small portions. The reaction proceeded with considerable heat evolution. The process was regulated so that the temperature of the reaction mixture did not exceed 0°. When all the sodium ethylate had been added, the contents of the flask were stirred for 30 minutes at − 10° and for 1 hour at room temperature. As a result of the reaction, a precipitate of sodium chloride was formed. After being stirred, the reaction mixture was treated with water and the ether layer separated and dried with baked $MgSO_4$. After removal of the ether, the residue was vacuum-distilled. The nitrile appeared as a colorless, mobile liquid with a weak smell. We obtained 10.6 g (53%).

B.p. 34-35° (1 mm), 41-42° (2 mm), d_4^{20} 0.937, n_D^{20} 1.4352, MR_D 34.82; calc. 34.50.
Found %: N 11.33. $C_7H_{11}ON$. Calculated %: N 11.20.

The nitrile of β,β'-diisobutylglycidic acid (II). 7.2 g of chloroacetonitrile, 18.6 g of isovalerone and 6.8 g of dry sodium ethylate were used. The reaction was performed in absolute ether. The nitrile was a colorless liquid with a weak smell. We obtained 6.4 g (35%).

B.p. 28-29° (2 mm), d_4^{20} 0.8475, n_D^{20} 1.4170, MR_D 53.89; calc. 52.97.
Found %: N 7.78. $C_{11}H_{19}ON$. Calculated %: N 7.73.

The nitrile of β,β'-diphenylglycidic acid (III). 10 ml of chloroacetonitrile, 20 g of benzophenone and 6.5 g of dry sodium ethylate were used. The reaction was performed in absolute ether. Vacuum distillation of the reaction mixture yielded a fraction, which crystallized after some time. We obtained 19.7 g (81%). After two recrystallizations from ethyl alcohol, the substance appeared as colorless crystals with m.p. 72°.

Found %: C 81.32; H 5.08; N 6.51; O 7.58. $C_{15}H_{11}ON$. Calculated %: C 81.45; H 4.98; N 6.34; O 7.24.

The nitrile of β,β'-dibenzylglycidic acid (IV). 5.0 ml of chloroacetonitrile, 16.0 g of freshly distilled dibenzyl ketone and 5.0 g of dry sodium ethylate were used. The reaction was performed in absolute ether. The nitrile appeared as a slightly yellowish, oily liquid. We obtained 11.8 g (65%).

B.p. 197° (10 mm), d_4^{20} 1.0966, n_D^{20} 1.5667, MR_D 74.00; calc. 73.47.
Found %: N 5.58. $C_{17}H_{15}ON$. Calculated %: N 5.62.

The nitrile of β,β'-di-p-tolylglycidic acid (V). 3.2 ml of chloroacetonitrile, 13.4 g of di-p-tolyl ketone and 3.0 g of dry sodium ethylate were used for the reaction. The reaction was performed in absolute ether. The reaction product was isolated by vacuum distillation. We obtained 12.6 g (80%). After recrystallization from ethyl alcohol, the substance had m.p. 108°.

Found %: N 5.66. $C_{17}H_{15}ON$. Calculated %: N 5.62.

Acid hydrolysis of the nitriles of β-pentamethylene- and β,β'-dimethylglycidic acids. 5 ml of the nitrile of β-pentamethyleneglycidic acid, 15 ml of water, 5 ml of ethyl alcohol and 0.5 ml of concentrated sulfuric acid were heated for 10 hours on a boiling water bath in a sealed ampule until a homogeneous mass was obtained. The hydrolyzate was neutralized with $BaCO_3$ and steam-distilled. As a result, we obtained hexahydrobenzaldehyde with b.p. 161°, d_4^{20} 0.9390, n_D^{20} 1.4667. A 2,4-dinitrophenylhydrazone with m.p. 142° was prepared. A mixed melting point with the 2,4-dinitrophenylhydrazone of an authentic sample of hexahydrobenzaldehyde was not depressed. The aldehyde yield was determined quantitatively by oximination. The aldehyde yield equaled 63%. We should also add that we isolated $(NH_4)_2SO_4$, formed as a result of saponification of the nitrile group.

The nitrile of β,β'-dimethylglycidic acid was hydrolyzed similarly. In this case, less sulfuric acid was used; one drop of concentrated sulfuric acid was used for 5 ml of an aqueous alcohol solution of the nitrile. The percent of aldehyde formed was determined by oximination. The aldehyde yield equalled 65%.

Raman spectrum of β,β'-dimethylglycidonitrile, containing traces of the α-chloronitrile of 2-methylcrotonic acid. (The intensities of the lines were evaluated visually).

328 (2), 360 (1), 433 (1), 477 (1), 543 (1), 696 (2), 783 (2), 909 (2), 1032 (1), 1089 (2), 1243 (1), 1298 (1), 1393 (1), 2245 (10), 2935 (1), 2986 (1).

The spectra were plotted on a Zeiss spectrograph with a slit width of 0.008 mm and an exposure of 3 hours.

Raman spectrum of β-pentamethyleneglycidonitrile (the intensities of the lines were evaluated visually).

216 (2), 294 (3), 368 (1), 475 (3), 557 (2), 632 (1), 679 (3), 708 (2), 787 (3), 808 (0.5), 831 (3), 865 (2), 914 (3), 1031 (2), 1093 (2), 1117 (2), 1200 (2), 1218 (2), 1273 (1), 1338 (1), 2245 (10), 2458 (1), 2955 (3).

The spectra were plotted on an ISP-51 spectrograph with a slit width of 0.004 mm and an exposure of 11 hours.

The fall in the basic characteristic frequency of the vibration oscillation of the cyclohexane ring from 802 to 708 cm^{-1} is probably explained by the strong +I-effect of the nitrile group, which could lead to a displacement of the electron densities of the carbon atoms of the cyclohexane ring.

SUMMARY

1. A study was made of the reaction of monochloroacetonitrile under the conditions of the Darzan reaction with some aliphatic, aliphatic-aromatic and aromatic ketones. It was shown that this reaction was quite convenient for the preparation of β,β'-disubstituted nitriles of glycidic acids.

2. 5 glycidonitriles which are not described in the literature, were synthesized and characterized.

3. It was established that Michler's ketone does not react with monochloroacetonitrile to form the corresponding glycidonitrile, which may be explained by the strong electron donor properties of the dimethylamino group.

4. An investigation was made of the acid hydrolysis of β-pentamethyleneglycidonitrile; this gave the corresponding aldehyde, which indicates that the hydrolysis began with saponification of the nitrile group.

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TELOMERIZATION OF CHLOROPRENE IN THE REACTION WITH 1,3-DICHLOROBUTENE-2 UNDER THE ACTION OF $FeCl_3$. IV.

A. L. Klebanskii, A. G. Saladian and A. G. Barkhudarian

Telomerization, initiated by free radicals or ions, has attracted the attention of many investigators during recent years [1] as a method of organic synthesis and also as a method of preparing low-molecular polymers, which are used as plasticizers, film-forming materials etc.

In previous investigations [2], we studied the telomerization of 1,3-dichlorobutene-2 with chloroprene, isoprene and divinyl under the action of $FeCl_3$, with a large excess of dichloride; low molecular compounds were mainly formed. Determination of the fractional composition of the telomers, obtained with various diolefins, showed that fractions with the greatest degree of telomerization ($n = 19$ for the 1st fraction) were obtained with isoprene. Chloroprene formed lower-molecular compounds ($n = 6$ for the 1st fraction). Divinyl occupied an intermediate position. Thus, in telomerization reactions under the action of ionic catalysts, the activity of chloroprene is lower than that of other diolefins. This is in contrast to the relatively great reactivity of chloroprene (whose rate is 760 times greater than that of isoprene) in radical polymerization, for reactions in a homogeneous mass.

In order to establish the effect of the ratio of 1,3-dichlorobutene-2 (I) to chloroprene (II) on the molecular weight of the telomers formed in the presence of $FeCl_3$, in this work, we studied the telomerization over a wide range of molar ratios of (I):(II)— from 2:1 to 1:500. This was not only of theorectical interest, but had a certain practical value. The chloroprene distillate and especially the undistilled crude material contain traces of dichloride and $FeCl_3$. The latter is formed as a result of the reaction of impurities with readily ionizable chlorine (4-chlorobutadiene-1,2, 1,3-dichlorobutene-2 and some dimers), contained in the chloroprene, with the material of the apparatus. The presence of dichloride and $FeCl_3$ in the chloroprene may cause the formation of a certain amount of low-molecular polymers during the distillation or during long storage. Preliminary experiments also showed that these impurities cause a change in the molecular weight and the plasticity of chloroprene polymers during polymerization in a homogeneous mass. In emulsion polymerization, these impurities did not have any noticeable effect on the process and the properties of the polymers, due to hydrolysis of the $FeCl_3$ and losses in catalytic activity. The results of experiments at various ratios of dichloride to chloroprene are presented in Table 1 and in Figs. 1-4.

The molecular weight of polymers with molecular weight of 5000 and less was determined cryoscopically in benzene and compared with the value found viscosimetrically. By comparison of the data obtained by the two methods, the relation between the viscosity and the molecular weight was expressed in the form of the power function $M = a[\eta]^b$ or $\lg M = \lg a + b \lg [\eta]$. This gave the following values for the constants.

a) At an $FeCl_3$ concentration of 0.5 mole % $\lg a = 3.8390$, $b = 1.03297$.
$\lg M = 3.8390 + 1.03297 \lg [\eta]$

b) At an $FeCl_3$ concentration of 1 mole % $\lg a = 3.8972$, $b = 1.0945$.
$\lg M = 3.8972 + 1.0945 \lg [\eta]$.

As is shown, the corresponding values of the constants agree closely in the two cases. Using these formulas, we calculated the molecular weights of polymers, for which these values were more than 5000.

The characteristic viscosities of various polymer homologs are presented in Figs. 1 and 2.

TABLE 1

Dependence of Yield and Mean Molecular Weight of Polymer on the Ratio of the Starting Materials (Duration of experiments 48 hours, temperature 50°, $FeCl_3$ concentration 0.5 mole % in series I and 1 mole % in series II)

	Experiment No.	Molar ratio of dichloride to chloroprene	Yield of polymer on total monomers (in %)	Percent chlorine in polymer		Percent saponifiable chlorine in polymer		Characteristic viscosity $\eta_{sp}/(c \to 0)$	Mean molecular weight*			Calculated empirical formula	Calculated mean molecular weight from empirical formula
				found	calculated	found	calculated		viscosimetrically	cryoscopically in benzene	by saponified chlorine		
Series	1	2 : 1	1.96	44.98	45.43	8.72	9.11			412.0	407	$C_{16}H_{21}Cl_3$	390.5
	2	2 : 1	3.62	44.75	44.46	7.72	7.41			473.5	460	$C_{20}H_{26}Cl_6$	479.0
	3	1 : 2	4.33	44.22	44.46	7.51	7.41			489.5	459.8	$C_{20}H_{26}Cl_6$	479.0
	4	1 : 5	6.23	43.10	42.29	5.21	5.41	0.108	715	693.0	682.0	$C_{28}H_{36}Cl_8$	656
	5	1 : 50	7.45	42.0	42.62	3.98	4.26	0.135	837.5	840.3	882.3	$C_{36}H_{16}Cl_{10}$	833
	6	1 : 100	8.21	41.75	42.00	3.07	3.23	0.167	1097.0	1085.0	1156.0	$C_{48}H_{61}Cl_{13}$	1098.5
	7	1 : 500	9.25	38.47	39.4	0.61	0.70	0.722	4920.0	5065.5	5038.0	$C_{224}H_{281}Cl_{57}$	5043
Series	1	1 : 2	5.11	44.12	43.79	6.72	6.25			542.5	527.6	$C_{24}H_{31}Cl_7$	567.5
	2	1 : 5	7.45	43.04	42.37	3.92	3.85	0.142	933.0	891.5	905	$C_{40}H_{51}Cl_{11}$	921.5
	3	1 : 50	10.35	41.85	41.34	2.00	2.07	0.243	1684.0	1670.0	1775	$C_{76}H_{96}Cl_{20}$	1718.0
	4	1 ; 100	12.7	39.82	40.49	1.30	1.32	0.364	2620	2615.5	2719	$C_{120}H_{151}Cl_{31}$	2690.5
	5	1 : 500	15.54			0.64	0.69	0.708	5420	5125	5550	$C_{232}H_{291}Cl_{59}$	5167
	6	1 : 1000	16.83	Not determined				1.043	8275				

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*Determined after the polymers had been purified by solution in benzene and precipitation with methyl alcohol twice and then dried in vacuum in nitrogen.

TABLE 2

Solution concentration (g in 100 ml of benzene)	Flow time (sec)	Relative viscosity (η_{rel})	Specific viscosity (η_{sp})	Reduced viscosity $\eta_{sp}/(c \to 0)$
0.8709	97.6	1.5724	0.5424	0.175
0.705	94.4	1.1143	0.1143	0.1621
0.558	91.8	1.0838	0.0838	0.1507
0.4484	89.3	1.0861	0.0661	0.1476

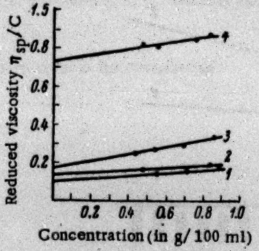

Fig. 1. Characteristic viscosities of solutions of polymer homologs, obtained with an $FeCl_3$ concentration of 0.5 mole %. Value of $\eta_{charact.}$: 1) 0.108 (expt. 4); 2) 0.135 (expt. 5); 3) 0.157 (expt. 6); 4) 0.722 (expt. 7).

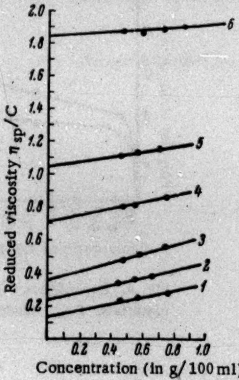

Fig. 2. Characteristic viscosities of solutions of polymer homologs, obtained with an $FeCl_3$ concentration of 1 mole %. Value of $\eta_{charact.}$: 1) 0.142 (expt. 2); 2) 0.243 (expt. 3); 3) 0.364 (expt. 4); 4) 0.7 8* (expt. 5); 5) 1.043 expt. 6); 6) 1.85 (expt. 7).

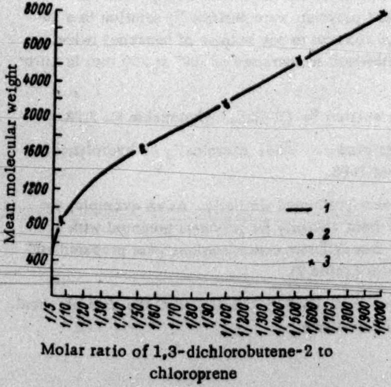

Fig. 3. Dependence of mean molecular weight of polymer on ratio of starting materials (the $FeCl_3$ concentration equaled 1 mole %).
1) Calculated theoretically; 2) determined by hydrolyzable chlorine; 3) determined cryoscopically in benzene.

The data presented in Table 1 show that with a decrease in the ratio of 1,3-dichlorobutene-2 to chloroprene, both the yield and the mean molecular weight of the polymer formed increase. This is illustrated by the curves in Figs. 3 and 4.

The presence of hydrolyzable chlorine in all the fractions and the increase in the content of it as the molar ratio of 1,3-dichlorobutene-2 to chloroprene increases, and also the agreement between the molecular weights determined by the hydrolyzable chlorine and by other methods indicate the following scheme for the telomerization process:

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*As in Russian. Probably is 0.708 – Publisher's note.

$$RCl + FeCl_3 \rightarrow R^+FeCl_4^-$$
$$R^+FeCl_4^- + D \rightarrow RD^+FeCl_4^- \rightarrow RDCl + FeCl_3$$
$$RD^+FeCl_4^- + D \rightarrow RD_2^+FeCl_4^- \rightarrow RD_2Cl + FeCl_3$$
$$RD_{n+1}^+FeCl_4^- + D \rightarrow RD_n^+FeCl_4^- \rightarrow RD_nCl + FeCl_3$$
$$R = CH_3CCl{=}CHCH_2Cl \text{ and } D = CH_2{=}CClCH{=}CH_2$$

The reaction studied can also be considered as a stepwise copolymerization of chloroprene and the dichloride, initiated by the cation-active catalyst $FeCl_3$.

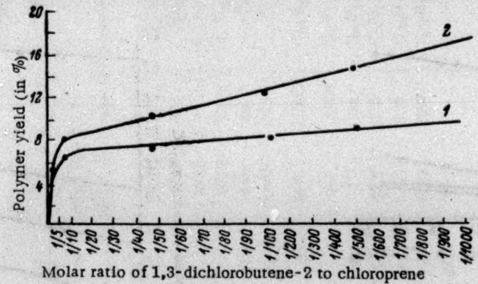

Fig. 4. Dependence of polymer yield on ratio of starting materials. $FeCl_3$ concentration (in mole %): 1) 0.5; 2) 1.

EXPERIMENTAL

133.2 g of chloroprene (1.505 mole), 1.9 g of 1,3-dichlorobutene-2 (0.015 mole) and 1.23 g of $FeCl_3$ (0.5 mole %) were heated in a sealed ampule in nitrogen, freed from oxygen, at 50° for 48 hours. The reaction product was washed with 10% HCl to remove the catalyst and then with water and dried with $CaCl_2$. The unreacted chloroprene and dichloride were removed in vacuum. The residual polymers were purified by solution in a 10-fold excess of benzene and precipitation with methyl alcohol (1.5 volumes to one volume of benzene) twice. The precipitated polymers were dried to constant weight at a water-bath temperature of 100° at 100 mm in nitrogen and analyzed.

Found %: Cl 41.75, hydrolyzable Cl 3.07. $C_{48}H_{61}Cl_{13}$. Calculated %: Cl 42.0, hydrolyzable Cl 3.23.

Mean values of molecular weight found: cryoscopically (in benzene) 1085; chemically by hydrolyzable chlorine 1156; viscosimetrically 1097. $C_{48}H_{61}Cl_{13}$. Calculated M 1098.

The other experiments and analyses presented in Table 1 were performed similarly. As an example, we present data on the determination of the mean molecular weight from viscosity for polymers prepared with a dichloride: chloroprene ratio of 1:500. Solutions in benzene at four different concentrations were prepared and examined. The viscosity was determined in an Ostwald viscometer (Table 2).

The characteristic viscosity, $\eta_{\text{charact.}} = 0.777$ (Fig. 1) was determined graphically from the data obtained. The characteristic viscosities of all the polymers were determined similarly.

SUMMARY

1. A study was made of the telomerization of chloroprene in the presence of 1,3-dichlorobutene-2 under the action of $FeCl_3$.

2. Investigation of the polymers obtained showed that 1,3-dichlorobutene-2 formed part of all the polymers in amounts which fell with a decrease in the molecular ratio of the dichloride to chloroprene; the mean molecular weights of the polymers increased correspondingly.

3. A satisfactory agreement was found between the molecular weights determined by the hydrolyzable chlorine, cryoscopically and viscosimetrically, and this confirms the scheme proposed for telomerization under the action of $FeCl_3$.

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* In Russian.

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ON THE ORDER OF ADDITION OF LITHIUM TO BIPHENYL

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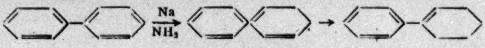
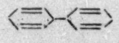
Schlenk and Bergmann [1] first showed that when an ethereal solution of biphenyl is shaken with lithium, the latter is almost quantitatively added to the biphenyl, a dilithium derivative being formed. On treatment of the latter with alcohol, dihydrobiphenyl is obtained; on treatment with carbon dioxide, dihydrobiphenylcarboxylic acid is formed. As in the catalytic hydrogenation of dihydrobiphenyl, cyclohexylbenzene was obtained, and when the dicarboxylic acid was boiled with acetic anhydride, the acid remained unchanged. Schlenk and Bergmann held that the addition of lithium to biphenyl occurs in the 1,4-position. Benkesser and co-workers [2] obtained cyclohexylcyclohexene-1 on reduction of biphenyl with lithium in a methylamine medium; on reduction of anisole [3] they obtained a mixture of 2,5- and 2,3-dihydroanisoles. The cited authors suggested that the addition of lithium to aromatic hydrocarbons occurs in the 1,4-position, and that the resulting quinoid system then isomerizes to a more stable conjugated system. Hückel and co-workers published two works on the reduction of biphenyl with sodium in liquid ammonia. In the first work [4] it was suggested that a conjugated double bond is initially formed, and one bond is then reduced.



Seventeen years later, Hückel [5] revised his conclusions. Proceeding from ultraviolet spectra, and also on the basis of the results of hydrogenation and the absence of an adduct with maleic anhydride, Hückel holds that the addition of sodium to biphenyl occurs in the 1,4-position in both rings, and the product obtained has one of the following structures:



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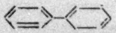
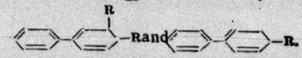
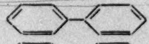


On reaction of dilithiumdihydrobiphenyl with alkyl halides [6] (C_4H_9Br, $C_6H_{13}Br$, sec-$C_8H_{17}Br$, $C_9H_{19}Br$ and $C_{10}H_{21}Br$), mono- and dialkyldihydrobiphenyls were obtained. Absorption bands were observed in the ultraviolet spectra of these hydrocarbons, which were similar in intensity and position to those in the spectra of biphenyl and phenylcyclohexene-1. On the basis of this we suggested that the hydrocarbons obtained may have the following structures:



Continuing this work, we conducted the present investigation for the purpose of determining the positions of addition of lithium to biphenyl in greater detail. In connection with this, the ultraviolet and infrared absorption spectra of the following hydrocarbons, synthesized by us, were obtained.

(I)



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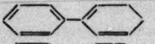

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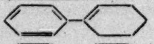
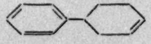
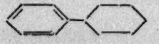


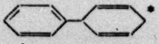
(IV)



(V)



(VI)



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The ultraviolet spectra were taken by the usual method in an ISP-22 spectrograph and SF-4 spectrophotometer, and the infrared spectra were obtained with an IKS-11 spectrometer equipped with LiF and NaCl prisms. The ultraviolet spectral data are shown in Fig. 1. On examining these data it may be seen that the spectra of

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* The given structure is assigned on the basis of Schlenk's conclusions (which, as will be shown later, are erroneous).

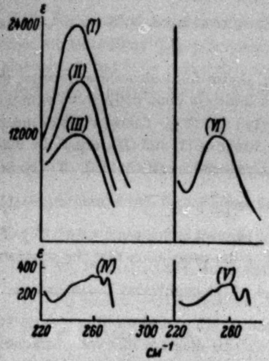
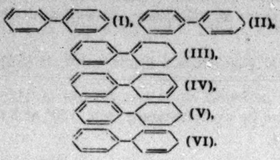


Fig. 1. Ultraviolet absorption spectra of the hydrogenation products of biphenyl. (Solutions in isooctane; ε is expressed in liters / mole · cm).



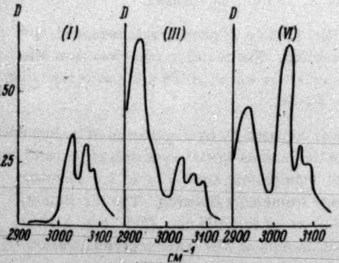
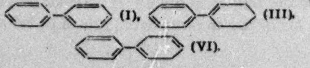
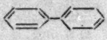
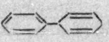
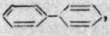
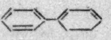
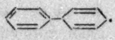


Fig. 2. Infrared absorption spectra in the 2900-3100 cm^{-1} region.

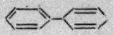
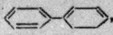
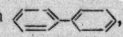


(I), (II), (III) and (VI) sharply differ from those of (IV) and (V). The spectra of the first compound contain one broad and very intense band without appreciable fine structure. The intensity (ε) of this band at the maximum (250 mμ) is 24,000 units for (I), 18,000 for (II), and about 12,000 for (III) and (VI). It follows from these data that a decrease in the number of conjugated bonds causes a corresponding decrease in the band intensity, and that the absorption-band intensity in(VI) is nearly the same as that in (III), i.e., in a compound in which one C=C bond is conjugated with a benzene ring. The spectra of (IV) and (V) resemble each other and differ little from those of the well-known monosubstitution products of benzene. The absorption bands have a pronounced fine structure with values of ε equal to 200-400 units.

The data given do not support the quinoid structure of the second ring in (VI), since in the case of the quinoid structure we would observe (in view of the absence of conjugation of the C=C bond with the benzene ring) a lower absorption-band intensity, approximating to that in the ultraviolet spectra of (IV) and (V). From the literature it is known [13] that the ultraviolet spectrum of an aromatic ring with a quinoid structure does not differ essentially from that of the cyclohexane ring; e.g., the ultraviolet spectra of tetralin and 1,4-dihydronaphthalene are similar. Therefore, taking into account the value of ε in the spectrum of (VI) (12,000), we may imagine its structure to be . General speaking, we may assume also the existence of a mixture of biphenyl and  or (II) and , or even  and .

In order to solve this problem we turned to the infrared absorption spectra. Spectra in the 2-15μ region were obtained for (I-VI) with a NaCl prism. We paid particular attention to the 3-3.5μ region, in which, as is generally known, the wave-numbers of the valence vibrations of the CH_2 and CH groups are located, and also to the 6-7μ region, where wave-numbers characteristic of the valence vibrations of the C=C group and the deformation vibrations of the CH_2 group are located. A LiF prism was used in the 3-4μ region.

The following facts were ascertained on examination of the infrared spectra. 1) In all spectra there are observed wave numbers characteristic of aromatic hydrocarbons containing a monosubstituted benzene ring, e.g., 1070, 1156, 1185, 1600 and 3030 cm^{-1}. 2) In the spectra of (I), (II), (III) and (VI) the C=C wave number, 1600 cm^{-1}, is decreased to 1590 cm^{-1}, as is usually observed on conjugation of multiple bonds; in (IV) and (V) this wave number retains its value, 1600 cm^{-1}. The difference between the spectra of (I), (II), (III) and (VI) and those of (IV) and (V) is observed in other regions; in the infrared spectra of (I), (II), (III) and (VI), for instance, bands at 910, 1017 and 1045 cm^{-1} are found, while in those of (IV) and (V) there is no band at 910 cm^{-1}, but bands at 1000, 1010 and 1030 cm^{-1} are observed.

As may be seen, the result obtained is in conformity with the conclusion, drawn from ultraviolet spectra, that the synthesized hydrocarbons may be divided into two groups: those having a multiple bond conjugated with the benzene ring [(I), (II), (III) and (VI)] and those not having such conjugation [(IV) and (V)]. Comparison of spectra reveals further that the infrared spectrum of (VI) does not contain the intense bands of (I) and (II), e.g., the 925 cm^{-1} band. This excludes the possibility of the presence of an admixture of biphenyl or (II) in (VI). The existence of the above-mentioned mixtures, as well as a mixture of  and , is also improbable because in the case of mixtures of a conjugated compound with an unconjugated one, broadening or splitting of the C=C band at 1600 cm^{-1} should be observed. The stated arguments lead to the conclusion that the structure of (VI) should have the form , i.e., phenylcyclohexadiene-1,4. This conclusion is also in conformity with the intensities of the CH_2 group vibration bands. In Fig. 2 are shown infrared absorption spectra in the 2900-3100 cm^{-1} region for compounds (I), (III) and (VI). It is evident from this diagram that the characteristic CH_2 group band located near 2930 cm^{-1} has negligible intensity in (I) ($D < 0.01$); its optical density is 0.7 in (III) and 0.45 in (VI). It follows from this that since (III) contains four CH_2 groups, (VI) will contain about (sic) two.

On the basis of all that has been said, it may be considered that the addition of lithium to biphenyl occurs in the 3,6-position. This type of structure is in accord with Schlenk and Bergmann's finding that no anhydride is formed by the dicarboxylic acid obtained, with Hückel's observation that no adduct is formed with maleic anhydride, and with our data on the very high intensity of the 250 mμ maximum for all mono-, as well as dialkyldihydrobiphenyls obtained by us.

EXPERIMENTAL

1. Phenylcyclohexane was prepared through the alkylation of benzene by cyclohexanol; b.p. 100° at 5 mm, n_D^{20} 1.5250. According to cited data [7]: b.p. 115° at 15 mm, n_D^{18} 1.5264.

2. Phenylcyclohexene-1 was prepared by dehydration of phenylcyclohexanol-1 over CH_3COOH and H_2SO_4; b.p. 114° at 5 mm, n_D^{20} 1.5679. According to cited data [8]: b.p. 124° at 14 mm, n_D^{20} 1.5692.

3. Phenylcyclohexadiene-1,5 was prepared by a cited method [9]. To 53 g of phenylcyclohexene-1, dissolved in 100 ml of ether, 55 g of bromine was added dropwise with cooling. The reaction mass was then left for two days at room temperature. After removal of the ether the hydrocarbon was distilled and was recrystallized twice from ethanol; m.p. 54-55°. According to cited data [9]: m.p. 53-54°.

4. Preparation of phenylcyclohexene-3. Cyclohexanediol-1,4 was prepared by hydrogenation of hydroquinone in dimethylcyclohexane solution over a Raney-nickel catalyst at 110-120° and an initial hydrogen pressure of 75 atm. By slow distillation of a mixture of 15 g of the carbinol and 150 ml of hydrobromic acid, 20 g of 1,4-dibromocyclohexane was obtained. The latter was separated into cis and trans isomers by freezing. The cis isomer, 15 g of which was obtained, had b.p. 80° at 5 mm and n_D^{20} 1.5408. According to cited data [10]: b.p. 111° at 13 mm, n_D^{20} 1.5448. The trans dibromide, of which 4 g was obtained, melted at 110° after recrystallization from petroleum ether. According to cited data [11], m.p. 113°.

To the Grignard reagent prepared from 2.4 g of magnesium, 16 g of bromobenzene, and 50 ml of ether was added 24.2 g of cis-1,4-dibromocyclohexane. After boiling for 30 hours the product was worked up in the usual way. There was obtained 18 g of phenyl-4-bromocyclohexane. When the latter was boiled with alcoholic alkali, phenylcyclohexene-3 was obtained; b.p. 85° at 4 mm, n_D^{20} 1.5350. According to cited data [12]: b.p. 98° at 11 mm, n_D^{20} 1.5440.

5. Preparation of dihydrobiphenyl by addition of lithium to biphenyl. Into a flask were put 40 g of biphenyl, 300 ml of ether, and 4 g of lithium, and also glass beads. This mixture was agitated in a shaker for 100 hours, after which the reaction product was decomposed with alcohol. The ethereal solution was washed with water and dried. After removal of the solvent the liquid dihydrobiphenyl obtained was distilled in vacuo. It had b.p. 85-86° at 4 mm. After the unreacted biphenyl was frozen out, the dihydrobiphenyl had f.p. (− 5)-(− 6°) n_D^{20} 1.5603, d_4^{20} 0.9925. Dihydrobiphenyl did not give an adduct with maleic anhydride.

SUMMARY

On the basis of a study of the ultraviolet and infrared spectra of phenylcyclohexene-1, phenylcyclohexene-3, phenylcyclohexadiene-1,5, phenylcyclohexane, and the hydrobiphenyl obtained through the dilithium derivative of biphenyl, it has been shown that the addition of lithium to biphenyl occurs not in the 1,4-position, as Schlenk and Bergmann assumed, but in the 3,6-position.

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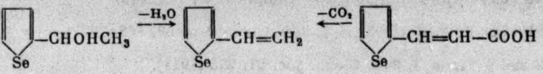
CHEMISTRY OF SELENOPHENE

XV. 2-VINYLSELENOPHENE

Iu. K. Iur'ev, N. N. Mezentsova and V. E. Vas'kovskii

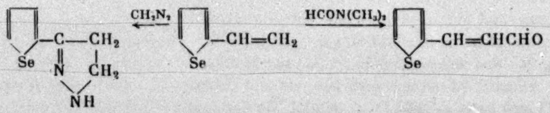
In the present work, in the course of an investigation in the field of selenophene chemistry, based on selenophene α-aldehydes [1-5], we prepared 2-vinylselenophene; of two possible routes for its synthesis, the catalytic dehydration of methyl-(selenienyl-2)-carbinol proved more convenient than the decarboxylation of β-(selenienyl-2)-acrylic acid, since it permitted the preparation of 2-vinylselenophene in considerably higher yield.



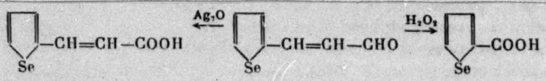
Methyl (selenienyl-2)-carbinol, as well as ethyl- and phenyl-(selenienyl-2)-carbinols, is formed smoothly by the reaction of selenophene-2-aldehyde with alkyl- and arylmagnesium halides.

On studying the effect of various dehydrating agents on methyl-(selenienyl-2)-carbinol, we found that in the presence of acidic agents — potassium bisulfate, p-toluenesulfonic acid, or an aluminosilicate cracking catalyst — or even potassium hydroxide, the 2-vinylselenophene formed is almost completely polymerized. On thermal dehydration 2-vinylselenophene is obtained in 50% yield. By vapor-phase dehydration in the presence of aluminum oxide at 200°, 2-vinylselenophene could be obtained in 80% yield. As regards the preparation of 2-vinylselenophene by the decarboxylation of β-(selenienyl-2)-acrylic acid, the attainable yield in this case is not over 40%.

On reaction with diazomethane, 2-vinylselenophene formed 4-(selenienyl-2')-pyrazoline, whereas on formylation with dimethylformamide in the presence of phosphorus oxychloride it gave β-(selenienyl-2-)-acrolein



On oxidation of β-(selenienyl-2)-acrolein with silver oxide in an alkaline medium, β-(selenienyl-2)-acrylic acid was obtained; oxidation of the former with hydrogen peroxide gave selenophene-2-carboxylic acid.



EXPERIMENTAL

Methyl (selenienyl-2)-carbinol. In a three-neck flask with stirrer, reflux condenser, and dropping funnel a solution of methylmagnesium iodide was prepared from 24 g (0.17 mole) of methyl iodide and 3.65 g (0.15 mole) of magnesium in 100 ml of absolute ether with cooling (snow and salt), and to it was added 21 g (0.13 mole) of selenophene-2-aldehyde in 50 ml of absolute ether during 30-40 minutes. The reaction mixture was heated for

1 hour in a water bath, left for 12 hours, and decomposed first with water and then with 10% acetic acid. The ether extracts were dried with potash; after the ether was driven off, the residue was twice distilled in vacuo. There was obtained 19.5 g (85%).

B.p. 100-100.5° (7 mm), 98-98.5° (6 mm), n_D^{20} 1.5792, d_4^{20} 1.5294, MR_D 38.07, $C_6H_8OSe F_2$. Calculated 38.94. Found %: C 40.85, 40.86; H 4.51, 4.42. C_6H_8OSe. Calculated %: C 41.15; H 4.60.

Ethyl (selenienyl-2)-carbinol. In the reaction described above, ethylmagnesium bromide, prepared from 8 g (0.074 mole) of ethyl bromide and 1.7 g (0.07 mole) of magnesium in 50 ml of absolute ether, was added to 10 g (0.063 mole) of selenophene-2-aldehyde in 50 ml of absolute ether. There was obtained 10.3 g (8%).

B.p. 111-111.5° (9 mm), n_D^{20} 1.5672, d_4^{20} 1.4512, MR_D 42.55. $C_7H_{10}OSe F_2$. Calculated 43.56. Found %: C 44.12, 44.28; H 5.06, 5.21. $C_7H_{10}OSe$. Calculated %: C 44.46; H 5.33.

Phenyl (selenienyl-2)-carbinol. Phenylmagnesium bromide, prepared from 11 g (0.07 mole) of bromobenzene and 1.7 g (0.07 mole) of magnesium in 50 ml of absolute ether, was made to react with 10 g (0.063 mole) of selenophene-2-aldehyde in 50 ml of absolute ether. There was obtained 9.6 g (64.5%).

B.p. 182-183° (9 mm); m.p. 60.61° (from ligroin); colorless crystals. Found %: C 55.96, 55.99; H 4.52, 4.59. $C_{11}H_{10}OSe$. Calculated %: C 55.71; H 4.25.

2-Vinylselenophene. a) Ten g (0.05 mole) of β-(selenienyl-2-)-acrylic acid (m.p. 114° [1]) and a small amount of phenyl-β-naphthylamine were slowly heated in a Wurtz flask in an oil bath at 180-200° in a current of nitrogen. The 2-vinylselenophene which distilled off was washed with water and dissolved in 10-15 ml of ether. The ethereal solution was dried with calcium chloride. After the ether was driven off, the residue was distilled in vacuo in a current of nitrogen. There was obtained 3.1 g (40%). 2-Vinylselenophene, obtained from a series of experiments, had the following constants after redistillation.

B.p. 95-95.5° (81 mm), 77-77.5° (40 mm), 69.5-70° (25 mm), n_D^{20} 1.6115, d_4^{20} 1.4460, MR_D 37.72. $C_6H_6Se F_3$. Calculated 36.95.

The residue in the flask was a dark, tarry mass.

b) A solution (35%) of methyl (selenienyl-2)-carbinol in benzene, containing a small amount of phenyl-β-naphthylamine, was heated and, at 30-40 mm pressure in a weak current of nitrogen, was passed through a tube (inner diameter 10 mm) filled with pieces of aluminum oxide (length of layer, 35 cm). The catalyzate was collected in a cooled receiver, and after the benzene (along with water) was driven off in a current of nitrogen, the residue was distilled in vacuo. The results obtained are given in the table.

In 6 hours without catalyst at 100°, 2-vinylselenophene polymerizes relatively slowly, being converted to a viscous, dark-red liquid.

Peroxides (benzoyl peroxide and hydrogen peroxide), and also potassium hydroxide, have a slight effect on the rate of polymerization on heating for 1 and 6 hours.

On heating for 1 hour in the presence of hydrochloric acid, vinylselenophene is converted to a viscous, dark-brown liquid; on heating for 6 hours, the product is a soft, dark-brown plastic.

4-(Selenienyl-2')-pyrazolinium oxalate. To a solution of 5.5 g (0.035 mole) of 2-vinylselenophene in 100 ml of absolute ether was added 200 ml of an ethereal solution of diazomethane [from 7.2 g (0.07 mole) of nitrosomethylurea], and the reaction mixture was heated for 12 hours in a water bath. After most of the ether was distilled off in vacuo, a saturated ethereal solution of anhydrous oxalic acid was added to the residue (~ 50 ml). There was obtained 4.5 g (53%); m.p. 113-114°.

Found %: C 39.16, 39.10; H 3.70, 3.75; N 11.07, 11.15. $C_{16}H_{18}O_4N_4Se_2$. Calculated %: C 39.40; H 3.72; N 11.45.

β-(selenienyl-2)-acrolein. To 7.13 g (0.10 mole) of dimethylformamide in a three-neck flask with stirrer, reflux condenser, and dropping funnel at 5° was added 15.2 g (0.10 mole) of phosphorus oxychloride. The mixture was stirred for 15 minutes at 20°, after which 35 ml of dichloroethane was poured in; then, at 5°, a solution of 14.2 g (0.096 mole) of 2-vinylselenophene in 35 ml of dichloroethane was slowly added. After heating in a water bath for 15 minutes the mixture was cooled, and a solution of 75 g of sodium acetate in 120 ml of water was added; the mixture was heated almost to boiling and cooled. The dichloroethane layer was drawn off, and the water layer was extracted with ether; after drying with anhydrous sodium sulfate and driving off the solvents the residue was distilled in vacuo in a current of nitrogen. There was obtained 9.2 g (55%).

Quantity of methyl (selenienyl-2)-carbinol (in g)	Quantity of benzene (in ml)	Temperature of experiment	Rate of introduction of the mixture (ml/min)	Yield of 2-vinylselenophene	
				(in g)	(in %)
5	15	300-305°	1.5	2.5	56
10	30	250-255	1.5	7.1	80
5	15	210-215	1.2	3.5	78
5	15	215-220	3.5	3.4	76
5	15	155-160	1.0	3.0	67
5	15	110-115	1.2	1.2	27

B.p. 155-155.5° (15 mm), 148-149° (9 mm), n_D^{20} 1.7006, d_4^{20} 1.5495, MR_D 46.13. $C_7H_6OSeF_3$. Calculated 41.59.

Found %: C 45.25, 45.33; H 3.36, 3.41. C_7H_6OSe. Calculated %: C 45.42; H 3.21.

β-(Selenienyl-2)-acrolein semicarbazone was prepared from 0.75 g of the aldehyde in 4 ml of alcohol, 0.75 g of semicarbazide hydrochloride, and 1.2 g of sodium acetate; m.p. 213-214° (decomp., from 90% alcohol).

Found %: N 17.26, 17.22. $C_8H_9ON_3Se$. Calculated %: N 17.35.

β-(Selenienyl-2)-acrolein thiosemicarbazone was prepared from 1 g of the aldehyde in 10 ml of alcohol, 0.5 g of thiosemicarbazide hydrochloride, and 0.1 ml of glacial acetic acid; m.p. 146-147° (from alcohol).

Found %: N 16.09, 16.02. $C_8H_9N_3SSe$. Calculated %: N 16.26.

β-(Selenienyl-2)-acrylic acid. To a mixture of 0.5 g of β-(selenienyl-2)-acrolein and 0.3 g of sodium hydroxide in 10 ml of water, alcohol was added until the aldehyde dissolved, and a saturated aqueous solution of 1 g of silver nitrate was then added dropwise. After standing for a day, filtration, concentration of the filtrate, and acidification with concentrated hydrochloric acid, 0.49 g (90%) of the acid was obtained; m.p. 139-140° (from water); a mixture test with known β-(selenienyl-2)-acrylic acid [1] showed no depression.

Selenophene-2-carboxylic acid. To 20 ml of 5% sodium hydroxide solution at 60° was added 1 g of β-(selenienyl-2)-acrolein and 15 ml of 3% hydrogen peroxide; the reaction mixture was acidified (to litmus) with concentrated hydrochloric acid and extracted with ether. After the ether was distilled off, 0.76 g (80%) of the acid was obtained; m.p. 119.5-120° (from water); a mixture test with known selenophene-2-carboxylic acid [1] showed no depression.

SUMMARY

1. The reaction of selenophene-2-aldehyde with alkyl- and arylmagnesium halides leads to the formation of secondary alcohols of the selenophene series. Methyl-, ethyl-, and phenyl (selenienyl-2)-carbinols, prepared in this way, are described for the first time.

2. The catalytic dehydration of methyl (selenienyl-2)-carbinol and the decarboxylation of β-(selenienyl-2)-acrylic acid both lead to 2-vinylselenophene.

3. The reaction of 2-vinylselenophene with diazomethane leads to the formation of 4-(selenienyl-2')-pyrazoline.

4. On formylation of 2-vinylselenophene with dimethylformamide, β-(selenienyl-2)-acrolein is obtained.

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DECOMPOSITION OF LIGNIN BY METALLIC SODIUM IN LIQUID AMMONIA

VII. CHROMATOGRAPHIC INVESTIGATION OF THE PHENOLS OBTAINED IN THE DECOMPOSITION OF LIGNIN

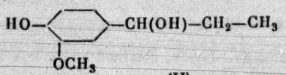
A. F. Semechkina and N. N. Shorygina

Earlier we established that metallic sodium in liquid ammonia solution decomposes lignin with the formation of monomeric phenols [1-3]. From the decomposition products of the copper-ammonia and hydrochloric acid lignins of spruce wood there were isolated dihydroeugenol and the phenolic alcohol $C_{10}H_{14}O_3$. The latter was obtained in the form of a sirup which gave a bis-phenylurethane and a dibenzoate; however, these had unsharp melting points. On oxidation of the sirup vanillic acid was obtained. It was suggested that the sirupy product contains 1-(4-hydroxy-3-methoxyphenyl)-propanol-1 or -2.

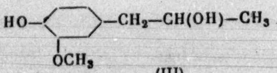
For a more detailed study of the phenolic decomposition products of lignin, formed by treatment of spruce-wood lignin with a solution of sodium in ammonia, paper chromatography was used. The lignin was prepared from wood according to the existing methods of Freudenberg [4] and Willstätter [5]. Treatment with a solution of sodium in liquid ammonia was carried out under the conditions described earlier [1], but with this modification: after the products of treatment of the lignin were decomposed with moist ether and with water, the aqueous, alkaline solution was not extracted with ether (to isolate dihydroeugenol), but was quickly acidified with dilute sulfuric acid, and only the acid solution was subjected to ether extraction. The mixture of phenols, thus obtained, was separated from acids by ether extraction from bicarbonate solution.

The purified sirupy mixture of phenols was chromatographed on paper by the descending method. The following solvents were used: 1) petroleum ether – benzene – water in the ratios 1 : 1 : 1; 2) petroleum ether – benzene – acetic acid – water in the ratios 1 : 1 : 0.25 : 1; 3) ligroin saturated with water. The phenols were developed with diazotized sulfanilamide. "Crab" (base under parchment) paper was used.

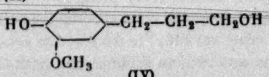
The composition of the phenols proved to be quite complex. On the chromatogram the lilac-colored spot of dihydroeugenol (I) is situated lowest of all (see diagram). Above it are the 1-(4-hydroxy-3-methoxyphenyl)propanols, of which all three possible isomers, guaiacyl-n-propanols-1, -2, and -3 (I, II, III), were found to be present.



(II)

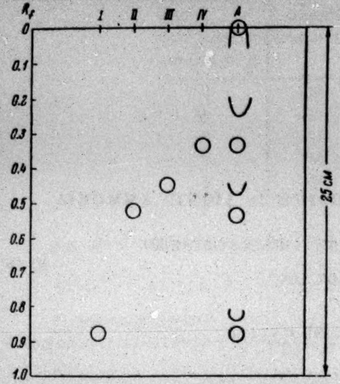


(III)



(IV)

The spot of substance (II), corresponding in position to the synthesized control substance, has an intense, rosy-orange color, whereas that of (IV) has a bright-lilac hue, corresponding to the color formed by synthesized substance (IV). The spot of (III), situated between those of (II) and (IV), is indistinct and has only a pale-lilac tint, while synthetic phenol alcohol (III) gives a bright-lilac spot in the same position. Above the spots for the group of the stated phenolic alcohols on the chromatogram of spruce-wood phenols, there are bright-orange spots, the nature of which has not yet been ascertained.



Paper chromatogram. Disposition of phenols from the hydrochloric-acid lignin of spruce wood.
I) Dihydroeugenol; II) 1-(4-hydroxy-3-methoxyphenyl)-propanol-1; III) 1-(4-hydroxy-3-methoxyphenyl)propanol-2; IV) 1-(4-hydroxy-3-methoxyphenyl)propanol-3; A) phenolic mixture from lignin.

In order to determine the behavior of the phenolic alcohols thus found, under the conditions of the decomposition of lignin, compounds (II), (III) and (IV) were treated with a solution of sodium in liquid ammonia under the conditions which we used for decomposing lignin.

The phenols which were isolated from the reaction mixture (after its decolorization) proved to be mainly the initial substances, with a very slight admixture of dihydroeugenol. On treatment with sodium in liquid ammonia solution, guaiacylacetone was quantitatively reduced to (III). Coniferyl alcohol gave dihydroeugenol in almost quantitative yield, as we had shown earlier [1].

Thus, under the conditions which we used for decomposing lignin, ketone groups in position 2 of the chain are not retained. However, considering that the yield of substance (III) from lignin is negligible, it may be assumed that there can only be very few CO groups in this position in lignin.

It might be mentioned that dihydroeugenol was repeatedly obtained from lignin in small quantities, e.g., in approximately 0.5% yield (based on the lignin taken), on dry distillation of corn husks in a hydrogen atmosphere in vacuo [6] and on heating sulfite caustics with alkali [7].

Phenol alcohol (IV) was found by paper chromatography in the ether-soluble fraction of maple hydrolignin [8].

The presence in lignin of side-chains with a hydroxyl group in the α-position with respect to the benzene nucleus (benzyl alcohol groups) has recently been indirectly proved several times by various investigators. A number of authors base their conclusion that these groups are present, on the sulfiting, and also the sulfiding, of lignin and type compounds [9]. Adler and Gierer [10] reach this conclusion by studying the methylation of lignin and type compounds by $CH_3OH + HCl$ at room temperature; the quantity of structural elements with free and etherified OH groups in the α-position with respect to the nucleus was estimated by the authors to be 50% of the total number of phenylpropane monomers for Braun's lignin.

Gierer [11], combining Braun's lignin with quinonemonochloroimine, concludes that in this lignin there must be one free group of the p-hydroxybenzyl alcohol type attached to every 7,8-phenylpropane link.

Use of the method of decomposition of lignin by sodium permitted a direct proof of the presence of these substances.

EXPERIMENTAL

1. Decomposition of lignin by sodium in liquid ammonia. Lignin, obtained by the hydrochloric acid method, had the composition (in %): C 62.81; H 6.05; OCH_3 15.20. Fifteen g of lignin was treated with 11.25 g of Na in liquid ammonia under the conditions used by us earlier. After decolorization of the blue solution (9 days) and removal of the ammonia, moist ether was added to the reaction vessel. Then, in a current of nitrogen, water was added, followed by dilute sulfuric acid until an acid reaction (with Congo) was obtained. The solution was extracted with ether. The phenols were separated from acids by ether extraction from a bicarbonate solution. Yield of phenols, 0.5 g. The phenols obtained were chromatographed.

2. Paper chromatography. On a 15 × 30 cm strip of ("Crab") paper, a spot consisting of an alcoholic solution of the phenols being investigated was placed at a distance of 4 cm from the edge, alongside spots of solutions of known monomers (I-IV) and developed for 6-12 hours with a moist mixture of benzene and petroleum ether (1:1 by volume) by the descending method. Then the strips were sprayed with a solution of diazotized

sulfanilamide in butyl alcohol and dried, after which they were sprayed with a semisaturated soda solution. The phenols were revealed in the form of colored spots.

3. Synthesis of monomers. 1-(4-Hydroxy-3-methoxyphenyl)propanol-1 was prepared by a cited method [12] through the reaction of vanillin (10 g) with ethylmagnesium bromide. Yield 8 g, m.p. 86° (from benzene), which corresponds to cited data [12].

Found %: C 65.78; H 7.91. $C_{10}H_{14}O_3$. Calculated %: C 65.93; H 7.69.

1-(4-Hydroxy-3-methoxyphenyl)propanol-3 was prepared by the reduction of ethyl hydroferulate with lithium aluminum hydride. Four g of the hydroferulic acid ester, dissolved in absolute ether (200 ml), were added dropwise to 4 g of lithium aluminum hydride, also dissolved in absolute ether (200 ml), during 1 hour with stirring, after which stirring was continued for 2 more hours. Then the reaction mass was discharged dropwise into ice. After acidification the carbinol was extracted with ether. M.p. 65°, yield 3.5 g.

Found %: C 65.71; H 7.74. $C_{10}H_{14}O_3$. Calculated %: C 65.93; H 7.69.

1-(4-Hydroxy-3-methoxyphenyl)propanone-2 was prepared by condensation of vanillin with nitroethane and subsequent reduction of the 4-hydroxy-3-methoxy-β-nitropropenyl-1-benzene obtained (1.6 g), by a cited method [13]. B.p. 155° (4 mm), yield 0.6 g.

1-(4-Hydroxy-3-methoxyphenyl)propanol-2* was prepared by reduction of the propanone-2 with lithium aluminum hydride. M.p. 52°.

4. Carrying out the reactions of monomers with metallic sodium in liquid ammonia.

a) To a solution of 1.75 g of coniferyl alcohol in 200 ml of liquid ammonia was added 1.75 g of metallic sodium. The reaction was continued for a week, the reaction mass being cooled with dry ice. Part of the sodium did not react during the stated period. The ammonia was removed by evaporation, and the mass left in the vessel was covered with moist ether and acidified with dilute sulfuric acid. From the ether extract, 1.5 g of an oily liquid was obtained. A chromatogram revealed the presence of dihydroeugenol together with a faint spot of 1-(4-hydroxy-3-methoxyphenyl)propanol-3.

b) 1-(4-Hydroxy-3-methoxyphenyl)propanol-1 was subjected to the same conditions. Chromatography revealed the presence of unchanged 1-(4-hydroxy-3-methoxyphenyl)propanol-1. There was also a faint spot of dihydroeugenol.

c) On the chromatogram, obtained after treatment of 1-(4-hydroxy-3-methoxyphenyl)propanol-3 with sodium in liquid ammonia, there was an intense spot of the original carbinol and a faint spot of dihydroeugenol.

d) One g of 1-(4-hydroxy-3-methoxyphenyl)propanone-2 was dissolved in 150 ml of liquid ammonia, and 1 g of sodium was added. The reaction was continued for 4 days, the reaction mass being cooled with dry ice. All the sodium reacted. The chromatogram showed the presence only of 1-(4-hydroxy-3-methoxyphenyl)propanol-2.

SUMMARY

On decomposition of spruce lignin by metallic sodium in liquid ammonia there is obtained a mixture of phenols, of which dihydroeugenol and 1-(4-hydroxy-3-methoxyphenyl)propanols-1 and -3 were identified through paper chromatography.

Part of the phenols obtained on decomposition of spruce lignin have not yet been identified.

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ON THE MECHANISM OF ACTION OF ACCELERATORS OF THE PROCESS OF SULFUR VULCANIZATION

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It was shown earlier that some accelerators of sulfur vulcanization, in particular ethanolamine, ethylene diamine and its derivatives, glucose and fructose, react with sulfur at 100-160° with the formation of hydrogen sulfide [1]. In connection with the postulated role of hydrogen disulfide as an intermediate product in this reaction its decomposition in solution in alkylbenzenes and olefins has been studied and it was shown that the process proceeds by a chain mechanism in which $HS^{\cdot}$ and $HS_2^{\cdot}$ radicals take part [2, 3]. In cumene, ethylbenzene and similar solvents the decomposition of H_2S_2 results in the formation of equivalent amounts of hydrogen sulfide and sulfur. In solution in α-olefins, which are effective free-radical acceptors, the formation of hydrogen sulfide is suppressed and the reaction products are mono-, di- and tetrasulfides. In β-olefins considerable amounts of hydrogen sulfide and sulfur are present in the reaction products in addition to the sulfides mentioned [2, 3].

In order to elucidate the mechanism of action of vulcanization accelerators it was necessary to study the composition of the products formed by their interaction with sulfur in various solvents and to compare it with the composition of the decomposition products of H_2S_2 in the same solvents. For this purpose we studied the reaction of monoethanolamine, ethylene diamine and fructose with sulfur in pentenes-1 and -2, cyclohexene, isoprene, α-methylstyrene, styrene, ethylbenzene and a rubber solution, at 130-160°. The process was characterized by the yield of hydrogen sulfide, and in the case of the reaction of monoethanolamine with sulfur in pentenes-1 and -2, all the main reaction products were isolated and characterized. Table 1 shows the data on the yield of hydrogen sulfide from the interaction of sulfur with the vulcanization accelerators and also from the decomposition of hydrogen disulfide in various solvents.

From the data presented in Table 1 it is seen that the yield of hydrogen sulfide from the interaction of monoethanolamine, ethylene diamine and fructose with sulfur in ethylbenzene is near to the theoretical in a number of cases. On conducting the reaction in α-olefins or rubber solution the yield of hydrogen sulfide falls to 0. In β-olefins, the double bond of which is less reactive towards free radicals [4], 20-40% of the theoretical amount of H_2S is evolved. Similar results are obtained for the decomposition of hydrogen disulfide.

In Table 2 experimental results are presented for the composition of the reaction products of sulfur and monoethanolamine in solution in pentenes-1 and -2. Here again the results of experiments on the decomposition of hydrogen disulfide are presented for comparison.

From the data of Table 2 it is seen that the interaction of sulfur with the vulcanization accelerators in an olefinic medium and also the decomposition of H_2S_2 in olefins, results in the formation of saturated sulfides. The yields of diamylmonosulfide from the reaction in pentene-1 (29%) and in pentene-2 (13%) are in good agreement with the yields of the monosulfide from the decomposition of H_2S_2 in the same solvents. The yields of diamyldisulfide in the products from the reaction of sulfur with the accelerator both in pentene-1 (30%) and in pentene-2 (9%) are higher than those from the decomposition of H_2S_2. There are substantial differences also in the yields of diamyltetrasulfide. In the reaction product in pentene-2 the yield of the tetrasulfide is 8% as against 19% for the decomposition of H_2S_2.

The comparatively low yields of tetra- and polysulfides in the cases examined is explained by the presence in the system of a considerable quantity of compounds with sulfhydryl groups (mercaptans, H_2S, H_2S_2). As is known, free aliphatic radicals react quantitatively with sulfur to form the corresponding polysulfides.

$$R\cdot + S_8 \rightarrow RS_n\cdot \rightarrow RS_mR.$$

TABLE 1

Yield of H_2S on Reaction of Sulfur with Vulcanization Accelerators and from the Decomposition of H_2S_2 in Various Solvents

Concentration of sulfur 0.315 g atoms/liter. Ratio of components: 1 atom of S per mole of accelerator. Concentration of H_2S_2 1.01-1.18 g moles/liter

Solvent	Reagent	Temperature	Reaction time	Yield of H_2S* (in %)
Ethylbenzene	Ethylenediamine + S	140°	1	30.0
		140°	8	66.5
	Fructose + S	160	8	48.5
	Monoethanolamine + S	143	1	38.8
		143	9	97.7
	H_2S_2	70	12	98.0
5% solution of SKS-30 rubber in ethylbenzene	Ethylenediamine + S	140	1	0**
		140	5	0**
	Fructose + S	160	1	0**
		160	5	0**
	Monoethanolamine + S	140	1	0**
		140	5	0**
	H_2S_2	70	15	0**
α-methyl styrene	Ethylenediamine + S	140	8	0
	Fructose + S	160	10	0
	Monoethanolamine + S	140	6	0
Styrene	H_2S_2	70	1	5.0
		70	5	5.0
Pentene-1	Monoethanolamine + S	130	10	0
	H_2S_2	130	10	5.2
		50	15	9.2
Pentene-2	Monoethanolamine + S	130	10	41
	H_2S_2	50	15	42
Cyclohexene	Monoethanolamine + S	130	10	23
	H_2S_2	50	15	58

When sulfur is present at the same time as mercaptans or hydrogen sulfide, of the two concurrent reactions: 1) $R\cdot + S_8\cdot \rightarrow RS_mR$ and 2) $R\cdot + R'SH\ (H_2S,\ H_2S_2) \rightarrow RH + R'S\cdot\ (HS\cdot,\ HS_2\cdot)$, the second takes place preferentially [5]. The absence of mercaptans from the reaction products conforms with the fact that reaction 2 proceeds considerably more rapidly than reaction 1.

It should be noted that under the given reaction conditions hydrogen sulfide does not add on to double bonds in the absence of free radicals [6], and sulfur reacts with olefins only to a small extent, forming higher polysulfides [7, 8].

The formation of the products obtained can be explained only by assuming that $HS\cdot$ and $HS_2\cdot$ radicals take part in the process [3].

The initial active centers are produced as a result of the reaction:

$$1)\ DH_2 + S_8 \rightarrow HSSH;\quad HSSH \rightarrow 2HS\cdot;\quad 2)\ DH_2 + HSSH \rightarrow DH + HS\cdot + H_2S$$

$(DH_2$ – vulcanization accelerator)

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* In the case of the decomposition of hydrogen disulfide the quantity of H_2S formed according to the reaction $H_2S_2 \rightarrow H_2S + \cdot S$ was taken as theoretical.

** Gel formation.

TABLE 2

Composition of Products from Reaction of Sulfur with Monoethanolamine and Decomposition Products of H_2S_2 in Pentenes-1 and -2.

Olefin	System	Temperature	Sulfur content in product (in % of initial)				
			H_2S	$(C_5H_{11})_2S$	$(C_5H_{11})_2S_2$	$(C_5H_{11})_2S_4$	$(C_5H_{11})_2S_n + S$
Pentene-1	Monoethanolamine + sulfur	130°	0	29	30	—	17.7
	H_2S_2	130	2.6	31	16.5	19.0	23.0
		50	4.6	31—39	11.8	25	18
Pentene-2	Monoethanolamine + sulfur	130	40.8	13.2	9	7.8	5
	H_2S_2	50	21.0	15	3	19	31

The role of the latter reaction is evidently small because in the presence of olefins only insignificant quantities of hydrogen sulfide are formed. The comparatively small yield of polysulfides provides evidence against the possibility of formation of significant quantities of HS_8H in reaction 1.

Hence the system consisting of sulfur and one of the vulcanization accelerators examined is a particular case of an oxidation-reduction initiated, radical process. In this case the oxidizing agent is sulfur and the reducing agents — the amines, hydroxycarbonyl, and certain other compounds.

The formation of hydrogen sulfide in the reaction between sulfur and vulcanization accelerators in ethylbenzene and other, similar solvents is evidently connected only with disproportionation of the free radicals $HS\cdot$ and $HS_2\cdot$ because hydrogen sulfide and sulfur are formed in equimolecular quantities on decomposition of H_2S_2 in these solvents [3]. The latter indicates that the $HS\cdot$ radical is unable to abstract hydrogen from the solvent. These radicals are very active in addition reactions to the double bonds of olefins, α-olefins being considerably more active than β-olefins. Hence the rules established in relation to the reactivity of internal and terminal double bonds towards aliphatic radicals, are confirmed also in the case of radicals with the active center on a sulfur atom.

EXPERIMENTAL

Pentene-1 was prepared from ethyl bromide and allyl bromide [9], b.p. 30°, n_D^{20} 1.3720.

Pentene-2 was prepared by dehydration of secondary amyl alcohol [10], b.p. 35.5° (736 mm), n_D^{20} 1.3790.

Cyclohexene was prepared by dehydration of cyclohexanol [11], b.p. 83.5°, n_D^{20} 1.4453.

The reaction between sulfur and monoethanolamine in solution in olefins was carried out in sealed ampoules in an atmosphere of dry nitrogen. The ampoule containing a weighed quantity of sulfur was evacuated a few times on an oil pump and the vacuum was let down with nitrogen. Weighed quantities of monoethanolamine and solvent were added against a countercurrent of nitrogen. The sealed ampoules were heated in an air thermostat at 130° with continuous shaking for 10 hours. At the end of the heating period the ampoules were cooled to −70°, opened and connected to a system for the absorption of hydrogen sulfide ($CdCl_2$ solution). For this purpose a current of nitrogen was passed through the solution at 0° and the CdS formed was determined iodometrically [12]. Divided portions of the solution after removal of H_2S were analyzed for mercaptan content.

The reaction mixture obtained consisted of a solution of sulfides in the olefin and a dark-red, resinous precipitate, soluble in water. The olefin solution of sulfides was decanted from the precipitate and treated as described in [3]. The precipitate was dissolved in water and analyzed for H_2S content (by reaction with $AgNO_3$) and for total sulfur content (by oxidation with bromine with subsequent precipitation of SO_4'' as $BaSO_4$).

Interaction of sulfur with monoethanolamine in pentene-1. 1.0 g of sulfur, 2.1 g of monoethanolamine and 35 ml of pentene-1 were taken. Concentration of S, 0.895 g atoms / liter. H_2S was not found in the reaction products.

The following were isolated: a) diamylmonosulfide 1.43 g (28.0% of initial sulfur)

B.p. 89-90° (12-13 mm), d_4^{15} 0.8452, n_D^{15} 1.4568.

Found %: C 68.66; H 11.54; S 19.47; monosulfide sulfur 98.8. Iodine number 0. M 164.177. $C_{10}H_{22}S$. Calculated %: C 68.96; H 12.64; S 18.39. M 174.

b) Diamyldisulfide 1.0 g (30% of initial sulfur).

B.p. 120-124° (12-13 mm), d_4^{15} 0.9620, n_D^{20} 1.5003.

Found %: C 62.11; H 10.12; S 30.0; disulfide sulfur 97.0. Iodine number 0, M 207.201, $C_{10}H_{22}S_2$. Calculated %: C 58.25; H 10.68; S 31.07. M 206.

c) The residue after removal of the mono- and disulfides by distillation, consisting of a mixture of polysulfides, was dissolved in toluene and refluxed with sodium sulfate solution for the determination of polysulfides and free sulfur [13]. The content of disulfide sulfur in the solution, after removal of free sulfur, was determined. The total quantity of sulfur found on analysis of the precipitate was 17.7% (including 7.7% disulfide sulfur).

d) In the hydrocarbon-insoluble residue from the ampoule ("resin") 14.0% of the initial sulfur was found after oxidation with bromine. The residue did not contain hydrogen sulfide.

The over-all sulfur balance of the products was 90%.

Interaction of sulfur with monoethanolamine in pentene-2. 2 g of sulfur and 4.2 g of monoethanolamine were taken. Concentration of S, 1.25 g atoms/liter.

The following were isolated: a) H_2S (gaseous and from the resin) 0.448 g (40.8%).

b) Diamylmonosulfide 1.39 g (13.2% of initial S).

B.p. 54-55° (2-3 mm), d_4^{15} 0.8428, n_D^{15} 1.4574.

Found %: C 68.10; H 12.57; S 18.46; monosulfide sulfur 101. Iodine number 0. M 168.5, 170.2. $C_{10}H_{22}S$. Calculated %: C 68.96; H 12.64; S 18.39. M 174.

c) Diamyldisulfide 0.57 g (9% of initial S).

B.p. 90° (2 mm), n_D^{15} 1.5056.

Found %: C 59.37; H 9.88; S 30.75; disulfide sulfur 95. Iodine number 0. M 201. $C_{10}H_{22}S_2$. Calculated %: C 58.25; H 10.68; S 31.07. M 206.

d) Diamyltetrasulfide 0.31 g (7.7% of initial S), b.p. 120-130° (2 mm).

Found %: C 46.47; H 7.91; S 46.02. $C_{10}H_{22}S_4$. Calculated %: C 44.44; H 8.15; S 47.70.

e) 5% of the sulfur was found in the residue after fractionation (including 1% disulfide sulfur).

f) In the "resin," in addition to hydrogen sulfide (20.8%), 9% of the initial sulfur was found.

SUMMARY

1. It is shown that the reaction of sulfur with various reducing agents that act as accelerators of the sulfur vulcanization process, proceeds through the intermediate stage of hydrogen disulfide, which decomposes with formation of $S\cdot$ and $S_2\cdot$ radicals.

2. On the basis of a study of the composition of the products formed by the interaction of sulfur with vulcanization accelerators and in the decomposition of hydrogen disulfide, in α- and β-olefins a suggestion is made about the mechanism of the formation of sulfur bonds in the vulcanization process and the role of accelerators in this process.

3. It is shown that terminal double bonds are considerably more reactive towards $HS\cdot$ and $HS_2\cdot$ radicals than are internal double bonds. It is shown that $HS\cdot$ radicals at 130° do not abstract hydrogen from aliphatic hydrocarbon solvents.

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**In Russian.

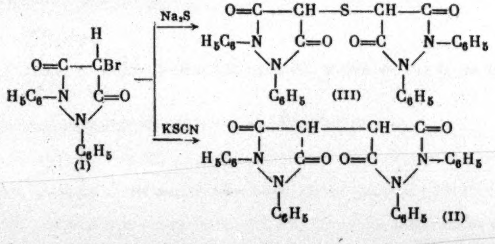
INVESTIGATIONS IN THE FIELD OF THE CHEMISTRY OF PYRAZOLIDINE

V. ON SOME ANOMALOUS REACTIONS OF 1,2-DIPHENYL-3,5-DIOXOPYRAZOLIDINE AND ITS HALOGEN AND THIOCYANOGEN DERIVATIVES

V. G. Pesin, A. M. Khaletskii and Teng Jun-hsiang

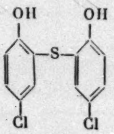
1,2-Diphenyl- and 4-n-butyl-1,2-diphenyl-3,5-dioxopyrazolidines and their halogen and thiocyanogen derivatives take part anomalously in certain reactions. It has already been reported [1] that on reacting 4-n-butyl-4-thiocyano-1,2-diphenyl-3,5-dioxopyrazolidine with alcoholic alkali, a substance containing no sulfur, and not the disulfide, is formed. Some anomalous reactions of 1,2-diphenyl-3,5-dioxopyrazolidine and its 4-bromo derivative are discussed in this communication.

On reacting 4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine (I) with potassium thiocyanate, 4-thiocyano-1,2-diphenyl-3,5-pyrazolidine is not formed but 4,4-bis-(1,2-diphenyl-3,5-pyrazolidine) (II), the structure of which we proved by independent synthesis (interaction of bismalonic ester and hydrazobenzene). Compound (II), as reported previously [1], is formed as a by-product together with the main product – bis-(1,2-diphenyl-3,5-dioxopyrazolidine) sulfide (III) – on reacting 4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine (I) with sodium sulfide or with triethylammonium diethylthiophosphate.



Comparison of these reactions (interaction of (I) with sodium sulfide and with potassium thiocyanate) suggests that the formation of (II) proceeds by a radical mechanism. The results obtained in attempts to carry out reactions between 4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine (I) with p-chlorophenol or with 2,2'-dioxo-5,5'-dichlorodiphenyl sulfide (IV) seem to us to be anomalies of the same type.

4-Bromo-1,2-diphenyl-3,5-dioxopyrazolidine (I) reacts with p-chlorophenol in the presence of metallic sodium or sodium carbonate in benzene; under these conditions a compound of the postulated structure (V) is formed.



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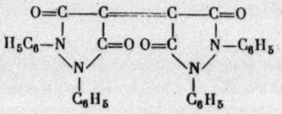

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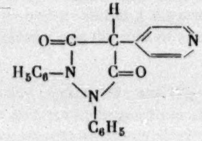
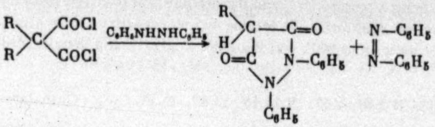


(VI)

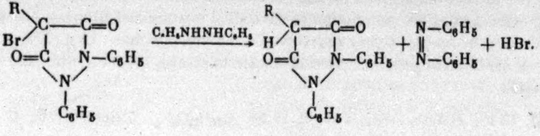
On conducting this reaction in the presence of pyridine another substance is also obtained, containing no halogen, of the composition $C_{20}H_{15}O_2N_3$ to which structure (VI) can be ascribed hypothetically.

Compound (VI) is formed when p-chlorophenol in this reaction is substituted by 2,2'-dihydroxy-5,5'-dichlorodiphenyl sulfide (IV) and also by the interaction of (I) with pyridine alone.

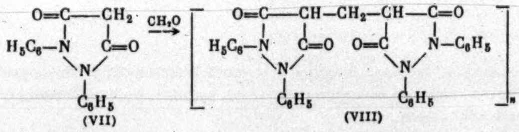
The presence of the double bond in compound (V) is indicated by the fact that it is not soluble in alkalis (i.e., it does not form an enol) and that it decolorizes bromine and potassium permanganate solutions. We suggest that these "anomalies" are very similar to the results, recently reported in the literature [2], of a study of the reaction between bromomalonyl chloride and excess hydrazobenzene. In this case 4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine is not formed, but 1,2-diphenyl-3,5-dioxopyrazolidine and azobenzene are formed.



The high lability of the bromine in the pyrazolidine ring leads to the fact that in the presence of hydrazobenzene, which possesses reducing properties, the bromine is split off and the hydrazobenzene is oxidized.



However, in the reactions that we carried out the bromine is not substituted by hydrogen but by a pyrazolidine ring, which can be explained by the strong tendency of the pyrazolidine radical to self-condensation when hydrogen is present on C_4. We also found this tendency to self-condensation in the reaction between 1,2-diphenyl-3,5-dioxopyrazolidine (VII) and formaldehyde; in this case methylene-bis-(2,3-diphenyl-3,5-dioxopyrazolidine), which we prepared by reacting methylene bismalonic ester with hydrazobenzene, is not formed, but a compound of the same composition, having different properties, possibly a polymer of the suggested formula (VIII) is formed.



(VII) (VIII)

EXPERIMENTAL

Investigation of the reaction between 4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine and potassium thiocyanate. 3 g of 4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine was added to a solution of 0.7 g of potassium thiocyanate in 15 ml of absolute alcohol at 30-40° with continuous stirring and the reaction mixture was heated in a flask under reflux on a boiling water bath, whereupon a precipitate appeared immediately. After heating for 4 hours and subsequent cooling, the precipitate was separated, washed with water, extracted with alcohol and recrystallized from chloroform. 1.8 g of material of m.p. 240-242° was obtained, consisting of white, small, needle-shaped crystals turning pink in the air and corresponding in melting point and other properties to 4,4'-bis-(1,2-diphenyl-3,5-dioxopyrazolidine) (II), which we prepared by condensing bismalonic ester with hydrazobenzene. A mixed melting point with the authentic sample showed no depression.

Found %: C 71.50, 71.89; H 4.40, 4.57; N 11.37, 11.32. $C_{30}H_{22}O_4N_4$. Calculated %: C 71.71; H 4.38; N 11.16.

Investigation of the reaction between 4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine and pyridine. 2.9 g of 4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine was heated with 15 ml of pyridine for 4 hours on a boiling water bath with continuous stirring. After 12 hours the precipitate that separated was filtered off and recrystallized from pyridine; 2.3 g (80%) of a compound of m.p. 253.5-254.5° was obtained. It consisted of white or yellowish crystals, insoluble in water and alkalis, of low solubility in ether and soluble in pyridine, alcohol, chloroform and acids.*

Found %: C 75.36, 75.45; H 4.56, 4.53; N 12.90, 12.85. $C_{20}H_{15}O_2N_3$. Calculated %: C 75.38; H 4.56; N 12.61.

Investigation of the reaction between 4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine with p-chlorophenol. A solution of 1.6 g of p-chlorophenol in 20 ml of dry benzene and 0.29 g of metallic sodium was heated in a flask under reflux until the sodium had dissolved, 2.9 g of 4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine was then added to the reaction mixture (containing a precipitate), and the mixture was refluxed for 8 hours. After filtration and removal of the benzene by vacuum distillation the residue was recrystallized from alcohol. 1.3 g (60%) of product was obtained, that did not melt up to 300°, was insoluble in alkalis and decolorized bromine and potassium permanganate solutions.

Found %: C 72.00, 72.33; H 4.34, 4.01; N 11.18, 10.87. $C_{30}H_{20}O_4N_4$. Calculated %: C 72.00; H 4.00; N 11.87.

4,4-Methylene-bis-(1,2-diphenyl-3,5-dioxopyrazolidine). 10 g of methylene bismalonic ester [3] and 11 g of hydrazobenzene were added to 1.6 g of metallic sodium in 50 ml of absolute alcohol. After heating on an oil bath at 120-130° the alcohol was distilled off and the reaction mixture was heated for 12 hours at 180-200° with continuous stirring. After adding 200 ml of water to the cooled mixture and filtering, the precipitate that separated on acidification with hydrochloric acid was recrystallized from alcohol; 12 g (77%) of product of m.p. 210-212° was obtained. It consisted of yellowish crystals, soluble in alkalis, alcohol, ether and chloroform, and insoluble in water and acids.

Found %: C 71.87, 72.17; H 4.41, 4.51; N 10.80, 10.56. $C_{31}H_{24}O_4N_4$. Calculated %: C 72.09; H 4.65; N 10.85.

Investigation of the reaction between 1,2-diphenyl-3,5-dioxopyrazolidine and formaldehyde. 0.5 ml of 40% formaldehyde solution was added to 3.4 g of 1,2-diphenyl-3,5-dioxopyrazolidine and the mixture was heated for 3 hours on a boiling water bath, with continuous stirring. The white precipitate formed was filtered off, washed with alcohol and extracted by heating with dichloroethane, from which it separated on cooling; 2.8 g of product, m.p. 246-248°, was obtained.

Found %: C 72.49, 72.47; H 5.30, 5.07; N 10.77, 10.27. $(C_{31}H_{24}O_4N_4)n$. Calculated %: C 70.09; H 4.65; N 10.85.

SUMMARY

1. A number of "anomalous" reactions involving 4-bromo-1,2-diphenyl-3,5-dioxopyrazolidine has been examined, in particular its reactions with potassium thiocyanate, pyridine, p-chlorophenol, etc.; the products formed did not contain sulfur or halogen.

2. It is shown that methylene-bis-1,2-diphenyl-3,5-dioxopyrazolidine is formed by reacting methylene bismalonic ester with hydrazobenzene.

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* Similar results were obtained when the reaction was carried out with either p-chlorophenol or 2,2'-dihydroxy-5,5'-dichlorodiphenylsulfide.

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SYNTHESIS AND STUDY OF THE POLYMERIZABILITY OF HALOGEN-SUBSTITUTED STYRENE DERIVATIVES

VII. TRICHLOROSTYRENE AND PENTACHLOROSTYRENE

N. A. Glukhov, M. M. Koton and Z. A. Koroleva

Up to the present time information on the synthesis of trichlorostyrenes is limited to a few patents [1] which claim their practical value in dielectrics and in the synthesis of Buna-S [2]. Pentachlorostyrene has also been little studied [3]. Conditions for the synthesis of the various trichlorostyrene isomers have not been studied nor has the effect of the structure of polyhalogenostyrene monomers on polymerizability and the properties of the polymers obtained. There is only one paper by Alfrey [4], where it is stated that in pentachlorostyrene, as a result of the presence of two chlorine atoms in the positions ortho to the vinyl group, retardation of the polymerization rate is observed.

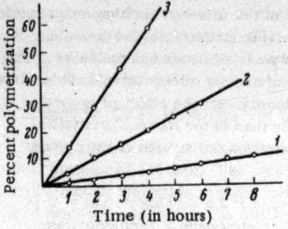

Fig. 1. Polymerization of 2,4,5-trichlorostyrene at 45° (1), 60° (2) and 75° (3).

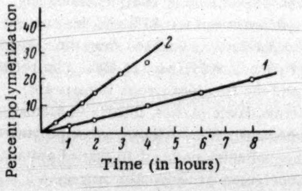

Fig. 2. Polymerization of 2,3,4-trichlorostyrene at 125° (1) and 150° (2).

With the object of filling this gap and continuing the systematic investigations in the field of substituted styrene we have developed syntheses of 2,4,5- and 2,3,4-trichlorostyrenes, which are not previously reported in the literature; found improved conditions for the preparation of pentachlorostyrene and studied their polymerization. Polymerization of the polyhalogenostyrenes was carried out by bulk polymerization using the dilatometric method. The ampoules, after charging with the monomers, were evacuated to $2 \cdot 10^{-1}$ mm for 2 hours and were then heated in an oil thermostat (accuracy, ± 0.5°). The polymer yield was determined by precipitating with methanol from benzene solution or by the bromination method; both methods were completely satisfactory with respect to accuracy of results.

The polymerization of 2,4,5-trichlorostyrene was studied at 45, 60 and 75° (Fig. 1), the polymerization of 2,3,4-trichlorostyrene – at 125 and 150° (Fig. 2) and the polymerization of pentachlorostyrene – at 125, 140 and 150° (Fig. 3).

From Fig. 1 it is seen that 2,4,5-trichlorostyrene polymerizes very readily, polymerization begins at 45°; at 75° in 2 hours, 29.5%, and in 3 hours, 43.3% conversion of monomer to polymer is reached. The isomeric 2,3,4-trichlorostyrene polymerizes with considerably more difficulty, giving at 125° in 2 hours about 5% of polymer and at 150°, in the same time, 15% of polymer. The polymerization of pentachlorostyrene (Fig. 3) proceeds slowly, forming 12% of polymer at 125° in two hours and 47% of polymer at 140°, in the same time. Comparison of the polymerization rates of polyhalogen-substituted styrene monomers with that of unsubstituted styrene (Figs. 4 and 5) shows that, with the exception of 2,4,5-trichlorostyrene, they polymerize considerably more slowly than styrene. The polymerization rates were in the following order: 2,4,5-trichlorostyrene > styrene > pentachlorostyrene > 2,3,4-trichlorostyrene.

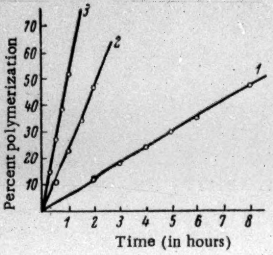

Fig. 3. Polymerization of pentachlorostyrene at 125° (1), 140° (2) and 150° (3).

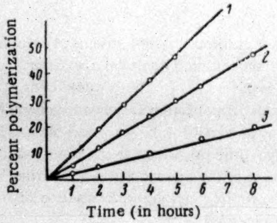

Fig. 4. Polymerization at 125° of styrene (1), pentachlorostyrene (2) and 2,3,4-trichlorostyrene (3).

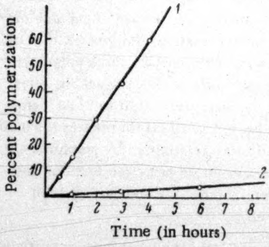

Fig. 5. Polymerization at 75° of 2,4,5-trichlorostyrene (1) and styrene (2).

In comparing the polymerization rates of the various halogen-substituted styrenes, the effect on polymerizability of the positions of the halogen atoms in the benzene ring of the substituted styrene should be noted. As has already been reported [5], the presence of a chlorine atom in the position ortho to the vinyl group in a chlorostyrene molecule considerably increases the polymerization rate in comparison with the para isomer. It was shown further [6] that with two chlorine atoms in the benzene ring of a dichlorostyrene the 2,5 position is the most advantageous for polymerization, the formation of a high-molecular polymer, with a high polymerization rate being observed. On passing to trichlorostyrene the still-greater effect of isomerism with respect to the positions of the three chlorine atoms in the monomer molecules should be noted. In this case the 2,4,5 position is the most advantageous. The presence of five chlorine atoms in the pentachlorostyrene ring, which add weight to the monomer molecule, and the presence of two chlorine atoms in the positions (2 and 6) ortho to the vinyl group cause considerable steric hindrance to the polymerization process and pentachlorostyrene polymerizes at little more than half the rate of unsubstituted styrene. Thus in examining the effect of the structure of chloro-substituted styrene monomers on polymerization rate, the increasing effect of isomerism of styrene substituted in the benzene ring, with increasing number of nuclear substituents should be noted. In the case of the trichlorostyrenes the effect of isomerism is manifested more strongly than in the monochlorostyrenes. With respect to polymerization rate all the chlorostyrenes studied form the series:

2,4,5-trichlorostyrene > 2,5-dichlorostyrene > 2,4-dichlorostyrene > 3,4-dichlorostyrene > 4-chlorostyrene > > styrene > 1,2,3,4,5-pentachlorostyrene > 2,3,4-trichlorostyrene.

Pentachlorostyrene was also bulk-polymerized in the presence of 0.1% of benzoyl peroxide at 125°; after heating for 3 hours the degree of conversion was 81% and the average molecular weight of the polymer, calculated from the relative viscosity and Billmeyer's function [7], was 28,500. The polymers of pentachlorostyrene and the trichlorostyrene isomers are transparent, brittle, thermoplastic masses, soluble in aromatic and halogenated hydrocarbons. The trichlorostyrene polymers have considerably higher softening points than that of polypentachlorostyrene. Copolymers of pentachlorostyrene with styrene and with methyl methacrylate, in the ratio 1:1, are transparent, colorless, thermoplastic masses.

EXPERIMENTAL

The synthesis of 2,4,5-trichlorostyrene was carried out according to the scheme

$$C_6H_5CH_3 \rightarrow C_6H_2Cl_3CH_3 \rightarrow C_6H_2Cl_3CHCl_2 \rightarrow C_6H_2Cl_3CHO \rightarrow C_6H_2Cl_3CHOH{-}CH_3 \rightarrow \\ \rightarrow C_6H_2Cl_3CH{=}CH_2.$$

Toluene was chlorinated in the nucleus with sulfuryl chloride in the presence of anhydrous aluminum chloride and sulfur polychloride according to Silberrad [8].

1680 g of sulfuryl chloride and 168 g of sulfur polychloride were added, over a period of 3 hours, to 368 g of toluene and 40 g of anhydrous aluminum chloride at 70°. The reaction mixture obtained was washed with hot water and distilled at ordinary pressure. The fraction boiling between 220 and 245°, which consisted of almost equal parts of 2,4,5- and 2,3,4-trichlorotoluene,was collected.

Yield 72%. 2,4,5-Trichlorotoluene of m.p. 82-83° (82.4° [8]) was isolated by fractional crystallization. 2,3,4-Trichlorotoluene of m.p. 40.5° (41° [8]) was isolated from the residual waxy mass.

An 87% yield of 2,4,5-trichlorobenzalchloride in the form of a colorless liquid of b.p. 275-280° (759 mm) was obtained from 200 g of 2,4,5-trichlorotoluene by chlorination with dry, gaseous chlorine at 215-225° under illumination by an electric lamp (500 w). After repeated redistillation the 2,4,5-trichlorobenzalchloride had the following characteristics. b.p. 153-155° (15 mm), d_4^{20} 1.5956, n_D^{20} 1.5992.

105 g of 2,4,5-trichlorobenzalchloride and 500 g of oleum containing 20% sulfur trioxide were placed in a round-bottomed flask fitted with a stirrer. The mixture was stirred for 30 minutes at room temperature and then poured on to ice. After washing with sodium carbonate solution and water,crystals of 2,4,5-trichlorobenzaldehyde were steam-distilled out.

The yield of pure 2,4,5-trichlorobenzaldehyde was 70%, m.p. 111-113° (112-113° [9]).

Dinitrophenylhydrazone-yellow crystals of m.p. 249.5-250°. Found %: N 14.33, 14.35. $C_{13}H_7O_4N_4Cl_3$. Calculated %: N 14.38.

Trichlorophenylmethylcarbinol was prepared by the Grignard reaction from 2,4,5-trichlorobenzaldehyde and methylmagnesiumbromide. A methylmagnesiumbromide solution was added dropwise to a suspension of 20.95 g of the aldehyde in ether. The reaction mixture was decomposed with ice and ammonium chloride solution. Yield of unrecrystallized carbinol, 95-100%. The carbinol was redistilled and the 130-135° (0.2-0.5 mm) fraction, which solidified in the receiver as a colorless, crystalline mass of m.p. 85-86°, was collected.

Found %: Cl 47.10, 47.30; OH 7.50, 7.53. $C_8H_6Cl_3OH$. Calculated %: Cl 47.23; OH 7.54.

The carbinol obtained was dehydrated in toluene solution over activated aluminum oxide at 350° and a residual pressure of 115 mm. The receiver was cooled in liquid nitrogen. The condensate obtained was washed with 10% sodium hydroxide solution and with saturated calcium chloride solution. The liquid was dried, the toluene removed and the residue distilled in vacuo. 2,4,5-Trichlorostyrene, a crystalline, colorless material, when distilled in vacuo at 90° (0.04 mm).

B.p. 35°, n_D^{36} 1.5923, d_4^{36} 1.3910, MR_D 50.45; calc. 49.72. Monomer content 99.5% (determined by bromination method).

The synthesis of 2,3,4-trichlorostyrene was similar to that of 2,4,5-trichlorostyrene. A 90% yield of 2,3,4-trichlorobenzalchloride was obtained from 2,3,4-trichlorotoluene by chlorination in the side-chain, and consisted of colorless crystals of m.p. 82-83° (from petroleum ether)(84° [9]). 2,3,4-Trichlorobenzaldehyde, m.p. 85.5-86° (86° [10]) was obtained in 90% yield by hydrolysis of the benzalchloride.

The 2,4-dinitrophenylhydrazone of the aldehyde had m.p. 263.5-237.5°.

2,3,4-Trichlorophenylmethylcarbinol was prepared in the usual way, by condensation of the aldehyde with methylmagnesiumbromide and decomposition of the complex formed, with water. Yield after two redistillations in vacuo at 123-125° (0.5-0.8 mm), 80%. The alcohol was a very viscous, colorless liquid.

B.p. 123-125° (0.5-0.8 mm), d_4^{20} 1.4696, n_D^{20} 1.5854.
Found %: Cl 46.95, 47.15; OH 7.48, 7.46. $C_8H_6Cl_3OH$. Calculated %: Cl 47.23; OH 7.54.

The alcohol was dehydrated as in the case of 2,4,5-trichlorophenylmethyl carbinol. A transparent, colorless, liquid was obtained, that solidified to a crystalline mass on cooling to −5°.

B.p. 80-81° (0.02 mm), n_D^{20} 1.5932, d_4^{20} 1.4020.

Found %: Cl 51.26, 51.30. $C_6H_2Cl_3CH=CH_2$. Calculated %: Cl 51.4. Monomer content 99.7% (determined by bromination method).

Synthesis of pentachlorostyrene. From the chlorination of toluene (184 g) with sulfuryl chloride (1485 g) in the presence of 1% of sulfur polychloride and anhydrous aluminum chloride, pentachlorotoluene was obtained in 89% yield after one recrystallization from benzene; m.p. 217.5-218° (218° [8]). The pentachlorotoluene obtained was converted to pentachlorobenzalchloride by chlorination at 220-225° with a current of dry chlorine and illumination of the reaction flask by an electric lamp (500 w). Yield after redistillation in vacuo, 85%, m.p. 118-119° (119.5 [11]).

Pentachlorobenzaldehyde was prepared by Newton's method as described by Ross [3]. Yield of crude product, 90-95%. After two recrystallizations from acetone the yield was 75-80% and the product had m.p. 198-198.5° (197-199° [3]).

Preparation of the carbinol from the aldehyde was carried out according to Lock [11], with some modifications. Instead of methyl iodide, methyl bromide was used in order to prevent dehydration of the carbinol during the course of the reaction, which can occur in the presence of traces of iodine. 14 g of fine-crystalline pentachlorobenzaldehyde was suspended in 120 ml of ether in a two-necked, round-bottomed flask and a filtered solution of Grignard reagent, prepared from 1.5 g of magnesium, 6.4 g of methyl bromide and 70 ml of ether, was added gradually. The mixture was heated for 4 hours, allowed to stand overnight and decomposed with saturated ammonium chloride solution; ether was added to the mixture, the ethereal layer was separated, washed, dried over calcium chloride and the solvent was distilled off. The residue was recrystallized from dilute alcohol yielding 7 g of methylpentachlorophenylcarbinol (47%) of m.p. 126° (126° [11]).

The carbinol obtained was dehydrated over activated aluminum at 310 ± 5° and 15-20 mm. The pentachlorostyrene was passed over aluminum oxide a second time in order to remove traces of the alcohol and the product was recrystallized from ethanol. The yield after passing twice over activated aluminum oxide and recrystallizing twice, was 42%. Pentachlorostyrene – long, thin needles of m.p. 113.5-114° (113.5-114.5° [3]).

SUMMARY

1. 2,3,4- and 2,4,5-trichlorophenylmethyl carbinol, and 2,3,4- and 2,4,5-trichlorostyrene have been synthesized and characterized for the first time. Improvements have been made in the conditions for the preparation of pentachlorostyrene of a high degree of purity.

2. The polymerization of tri- and pentachlorostyrenes has been studied over the temperature range from 45 to 150°.

3. It is shown that with respect to polymerization rate the polyhalogenostyrenes studied form the series: 2,4,5-trichlorostyrene > 1,2,3,4,5-pentachlorostyrene > 2,3,4-trichlorostyrene.

4. It has been found that the effect of isomerism of the substituents in the benzene ring on polymerization rate, increases with increasing numbers of chlorine atoms.

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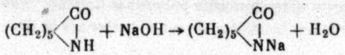
ON THE PROCESS OF FORMATION OF POLYAMIDE RESINS

VIII. THE QUESTION OF THE ALKALINE POLYMERIZATION OF ε-CAPROLACTAM

A. S. Shpital'nyi and N. S. Iablochnik

It has been found in work on the conversion of caprolactam to polymer in the presence of alkaline activators [1-4] that many reagents possess alkaline properties capable of activating the process of formation of polyamide macromolecules. In discussions on the nature of this process it has been noted that in its initial stages, as a result of interaction of the activator and the lactam, the alkaline salt of the lactam is formed, which is the real initiator that brings about the rapid course of the reaction in question. Indications of the formation of such salts can be found not only in the processes described where the activators are one or another of the alkali metals [2], but also in work on the polymerization of caprolactam with the help of alkaline agents such as sodium hydroxide, alkali metal acetates, etc. [3,4]. In the latter case some authors put forward the following scheme for the formation of the salt [3]

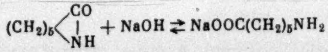


$$(CH_2)_5\left\langle\begin{matrix}CO\\|\\NH\end{matrix}\right. + NaOH \rightarrow (CH_2)_5\left\langle\begin{matrix}CO\\|\\NNa\end{matrix}\right. + H_2O \qquad (1)$$

and others limit themselves to an account of the way in which it takes part in polymer formation [4]. It has thus been assumed that in alkaline polymerization all the alkaline activators give rise to the formation of the alkali salt of the lactam, although indications of the possibility of such a transformation are cited only for the case where the activator is an alkali metal [2].

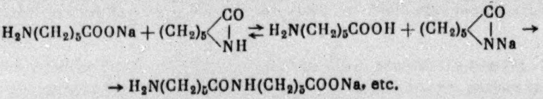
Our work shows that the reaction of caprolactam with alkali at a temperature of about 270° does not result in the formation of the alkali salt of the lactam but of the salt of aminocaproic acid. This follows from experiments on the reaction between alkali and caprolactam, with a considerable excess of alkali. It was considered that excess alkali would create conditions that would exclude the possibility of polymer formation and that would enable easily analyzable, low-molecular compounds to be obtained as end products. If the reaction mass should contain the alkali salt of the lactam in accordance with Eq. (1) it should be possible to extract the lactam unchanged after neutralization. In fact, in the reaction with sodium hydroxide either the salt of ε-aminocaproic acid or polymer was extracted from the reaction mass, depending on the conditions.

The formation of ε-aminocaproic acid in the reaction between sodium hydroxide and caprolactam is explained by reaction (2)



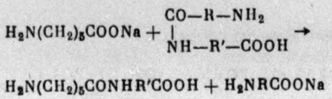
$$(CH_2)_5\left\langle\begin{matrix}CO\\|\\NH\end{matrix}\right. + NaOH \rightleftarrows NaOOC(CH_2)_5NH_2 \qquad (2)$$

It is quite possible that the compound HOOC $(CH_2)_5$NHNa is formed as an intermediate product and that because of its instability it immediately rearranges to the Na-salt of ε-aminocaproic acid. It was found in subsequent experiments that this salt is also capable of initiating the conversion of caprolactam to polymer. It should not be concluded from this that the caprolactam salt, and particularly its anion, does not take part in the process, because it would then be difficult to explain the rapid course of alkaline polymerization. Hence, if the experimental facts are taken into account in the polymer formation scheme and at the same time participation of the lactam salt is not excluded, the scheme can be depicted in the following form:



$$H_2N(CH_2)_5COONa + (CH_2)_5\left<\begin{matrix}CO\\|\\NH\end{matrix}\right. \rightleftarrows H_2N(CH_2)_5COOH + (CH_2)_5\left<\begin{matrix}CO\\|\\NNa\end{matrix}\right. \rightarrow$$

$$\rightarrow H_2N(CH_2)_5CONH(CH_2)_5COONa, \text{ etc.} \qquad (3)$$



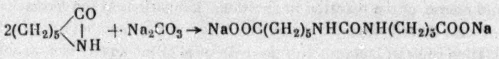
$$H_2N(CH_2)_5COONa + \begin{matrix}CO-R-NH_2\\|\\NH-R'-COOH\end{matrix} \rightarrow$$

$$\rightarrow H_2N(CH_2)_5CONHR'COOH + H_2NRCOONa \qquad (3a)$$

Reaction (3a) which brings about depolymerization or transamidation of the polymer [5] differs from the corresponding reaction of Griel [3] in that it is the aminocaproic salt (or its derivatives) and not the caprolactam salt (or its derivatives) that takes part.

Reactions (2), (3) and (3a) find confirmation in the conversion of the polyamide polymer to caprolactam by the action of sodium hydroxide at 270-300°, which is used as one of the methods of regeneration of the lactam from the waste products of the polyamide production [6].

If sodium carbonate reacts with caprolactam similarly to NaOH then the formation of the polymerization initiator when sodium carbonate takes part in the reaction can be depicted by the following scheme.



$$2(CH_2)_5\left<\begin{matrix}CO\\|\\NH\end{matrix}\right. + Na_2CO_3 \rightarrow NaOOC(CH_2)_5NHCONH(CH_2)_5COONa \qquad (4)$$

However, we have not yet succeeded in isolating the latter compound. It has already been stated above that by the action of an excess of even sodium carbonate on caprolactam, low-molecular compounds are not isolated from the reaction mass, but a water-insoluble polymer is isolated. The formation of a macromolecular compound is caused evidently by the low solubility of sodium carbonate in the caprolactam melt [3].

EXPERIMENTAL

Reaction of caprolactam with NaOH. A mixture of 2 g of powdered caprolactam and 1.2 g of powdered NaOH was heated in vacuo at 3 mm in an ampoule in a water bath for a few hours, to remove traces of moisture. The ampoule was then sealed and maintained at 280° for 2 hours. The melt was dissolved in water and the solution neutralized with 0.5 N sulfuric acid solution, after which it was evaporated on the water bath. The dry residue was treated with ether. No caprolactam was detected in the ethereal extract. The residue was treated with methyl alcohol. Precipitation of the alcohol solution with ether yielded a crystalline material which after recrystallization from methyl alcohol had m.p. 202°. A mixture with ϵ-aminocaproic acid melted without depression. Yield of ϵ-aminocaproic acid, 75.75%.

Reaction of the Na-salt of ϵ-aminocaproic acid with caprolactam. The Na-salt of ϵ-aminocaproic acid was prepared by addition of the calculated quantity of a standardized sodium hydroxide solution to a solution of ϵ-aminocaproic acid, and removal of the water by evaporation of the solution on the water bath.

A mixture of 0.0962 g of this salt and 0.856 g of caprolactam was placed in an ampoule and after displacement of the air by nitrogen the ampoule was sealed and maintained at 280° for 2 hours. After working up with ether and boiling with water for 15 minutes, the yield of resin was 80%. A molecular weight of 7,000 was found by titration of the resin in benzyl alcohol solution [7].

Reaction of caprolactam with sodium carbonate. A mixture of 3 g of powdered caprolactam and 3 g of powdered, anhydrous sodium carbonate was heated for 2 hours at 280° in a sealed ampoule. On treating the resulting melt with hot water for ½ hour, the major portion did not dissolve. The residue was filtered off and washed with water to neutral reaction. Yield of resin 65%. Molecular weight found, 1,035.

After neutralizing with sulfuric acid, the combined filtrate and water washings were evaporated on the water-bath. The dry residue was treated with ether. The residue after removal of ether from the extract consisted of a crystalline material that gave no melting point depression with caprolactam. The quantity of caprolactam extracted was 13.33%.

SUMMARY

1. It has been found that by the reaction of caprolactam with excess NaOH at 280° the alkali salt of ε-aminocaproic acid is formed.

2. A scheme is put forward for the reaction process between caprolactam and sodium hydroxide and for the conversion of caprolactam to polymer with the help of the alkali salt of ε-aminocaproic acid.

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N-ALKYLATED AND N-ARALKYLATED MORPHOLINE DERIVATIVES

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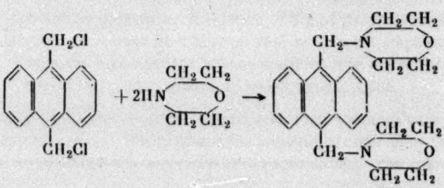
The use of morpholine in various branches of industry [1] has aroused interest in the study of the properties of its various derivatives, which contain the morpholine ring and which, in many cases, possess valuable properties. In recent years isolated representatives of such N-substituted morpholine derivatives in which the hydrogen of the morpholine ring nitrogen is substituted by various hydrocarbon radicals of both the aliphatic and aromatic series, have begun to find application. Compounds of this type are used at the present time for the production of surface-active and bactericidal substances [2, 3], as insecticides [4], as plant growth stimulators [5, 6], for the preparation of pharmacologically active substances [7-9], as antioxidant additives for lubricating oils [10], in the form of nitrites as inhibitors of corrosion by water and aqueous salt solutions [11], for the production of vat-dye leuco-compounds [12] and as catalysts in chemical reactions [13].

At the same time information in the literature on the preparation and properties of N-substituted derivatives of morpholine is very scanty and this considerably hinders investigation of the technical properties and further study of the possibility of using this class of compound. Examination of the individual cases of preparation of N-alkyl and N-aralkyl morpholine derivatives shows that the methods described can be divided into two groups: I) reactions in which morpholine is one of the starting materials, and II) reactions in which, in addition to condensation of the starting materials, cyclization must take place to form the morpholine ring. The reactions of morpholine with alkyl halides [7, 8, 14], or aldehydes [15, 16] and organomagnesium synthesis (through the intermediate formation of 4-morpholinomethylethyl ether) [17] belong to the first group. The following reactions belong to the second group: the reaction of primary amines with ethylene chlorohydrin [9], with dihalo-substituted ethyl ether (β, β'-diodoethyl ether [18, 19] or β,β'-dichloroethyl ether [20]) or with compounds of the type $RSO_2O(CH_2)n\ OSO_2R$ [21] and vapor-phase dehydration of N,N-bis-(2-hydroxyethyl)-alkylamines [22].

Comparison of these methods of preparation shows that with morpholine present the first group of reactions is the most practicable. However, data on the yields of the morpholine derivatives are almost absent from the literature.

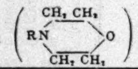
In the present work N-substituted morpholine derivatives were prepared by the reaction between morpholine and the respective alkyl or aralkyl halides for the purpose of studying their action on lubricating oils. The data in the literature on carrying out this reaction are very incomplete and data on the yields of the alkylated products are completely absent. Hence, in the process of conducting this work we selected the optimal conditions for preparing butylmorpholine; the other morpholine derivatives were then prepared in an analogous manner.

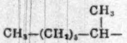
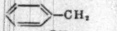
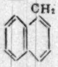
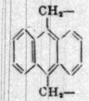
We synthesized the following morpholine derivatives under the conditions described below: ethyl-(II), propyl-(III), n-butyl-(IV), n-hexyl-(V), sec -n-octyl-(VI), n-octadecyl-(VII), benzyl-(VIII), α-naphthylmethyl morpholine (IX) and 9, 10-bis (morpholinomethyl)-anthracene (X). Compounds (VI) and (X) are not described in the literature.



(X)

TABLE 1

Physicochemical Properties of N-Substituted Alkylated and Aralkylated Morpholine Derivatives 

No. of compound	R		Boiling point (pressure in mm)	d_4^{20}	n_D^{20}	MR_D		Kinetic viscosity at 20° (in stokes)	Yield[2] (in %)
						found	calculated		
(I)	H	3.	127—128°	1.0030	1.4540	23.52	23.71	0.0271*	77
(II)	C_2H_5	4.	138—139	0.9115	1.4400	—	—	0.0129*	59
(III)	n-C_3H_7	5.	150—152	0.9110*	1.4471*	37.80	37.91	0.0175*	68
(IV)	n-C_4H_9	6.	175—177	0.9068*	1.4460*	41.95	42.52	0.0212*	75
(V)	n-C_6H_{13}	7.	215—217	0.8809*	1.4492*	52.08	51.76	0.0276*	84
(VI)	 $CH_3{-}(CH_2)_5{-}\overset{\overset{CH_3}{\vert}}{CH}{-}$		248—249*	0.8898*	1.4551*	60.63	60.99	—	76
(VII)	n-$C_{18}H_{37}$	8.	230—232 (10) M.p. 39	—	—	—	—	—	63
(VIII)		9.	138—140 (6)	1.0387	1.5302	52.29	52.77	—	65
(IX)		10.	178—180 (4)	1.1040*	1.6035*	70.71	70.80	0.3118*	49
(X)			M.p. 229—230*	—	—	—	—	(at 50°) —	46

Notes. 1) The asterisks denote data obtained by us that are not recorded in the literature. 2) Yields are calculated on the alkyl halide taken. 3) According to [22], b.p. 128-130°, d_4^{20} 0.9994, n_D^{20} 1.4545. 4) According to [19], b.p. 138-139°, d_4^{15} 0.9166, n_D^{20} 1.4400. 5) B.p. 43-46° 7 (mm) [17], 95-98° (22 mm) [16], 150° [3]. Yield from Grignard synthesis, 43.4% [17]. 6) B.p. 67-68° (10 mm) [22], 80-84° (15 mm) [16], 85-99° (25 mm) [15], 174° [4]. In [21] the m.p. of 213-214° is incorrectly quoted for butylmorpholine; its hydrochloride has this melting point. 7) B.p. 86-87° (6 mm) [17], 204° [3]. Yield according to [17], 59.7%. 8) B.p. 160-175° (0.3 mm) [20], 200° (4 mm) [3] m.p. 25° [8], 40° [3]. Yield [21] from condensation of octadecylamine with dichloroethyl ether, 88%. 9) B.p. 128-129° (13 mm) [22], 251° [7], d_4^{20} 1.0387 [19]; according to our results, n_D^{20} 1.0340, 1.5131 [9], 1.5256 [19]. Yield from synthesis by other methods, according to [17], 64.4%. 10) B.p. 185-190° (9 mm) [17]. Yield according to [14], 52%.

TABLE 2

Name of compound	pH
Morpholine	10.60
Ethylmorpholine	11.00
Propylmorpholine	9.90
Butylmorpholine	10.05

Some physicochemical constants were determined for the morpholine derivatives that we synthesized; in many instances these have not been previously recorded in the literature. Data on the properties of the N-substituted morpholine derivatives and the yields obtained in our experiments are given in Table 1. These figures give an indication of the variation in boiling point, density, refractive index and viscosity in the homologous series of N-alkylated and N-aralkylated morpholine derivatives. The pH value of a 0.1 M aqueous solution of some of the morpholine derivatives was measured with an LP5 potentiometer and a glass electrode. The results of these measurements are given in Table 2.

EXPERIMENTAL

We carried out experiments* on the preparation of butyl morpholine under various conditions: equimolar quantities of morpholine and butyl iodide or bromide were reacted together using potassium hydroxide as condensing agent and alcohol or benzene as solvent. The yield of butylmorpholine under these conditions was less than 50%. Increasing the time of heating to 10 hours did not increase the yield of reaction product. Carrying out the condensation with an excess of morpholine to combine with the hydrohalic acid (described in the case of the synthesis of α-naphthylmethylmorpholine [14]) was shown by our experiments to be very advantageous also for the preparation of the various alkylated morpholine derivatives, because the morpholine salt formed is insoluble in the majority of organic solvents, is easily separated from the main reaction product and the spent, excess morpholine can be regenerated. Carrying out the condensation without solvent enabled the reaction temperature to be increased to 130-140°, a saving to be made in the number of operations necessary and the yield of reaction product to be increased, particularly in the preparation of alkylated morpholine derivatives.

A description of the general method of preparation of N-substituted morpholine derivatives is given below. An account of the synthesis of compound (X) is also given because a different method was used for its isolation and purification.

Preparation of N-alkylated and N-aralkylated derivatives of morpholine. To morpholine (0.2 moles), prepared according to [23], placed in a round-bottomed flask fitted with a reflux condenser and dropping funnel, the alkyl halide (0.1 mole) was added gradually with external cooling and stirring, after which the reaction mixture was heated in an oil bath for 5 hours at 140°. At the end of the heating period the reaction product was extracted with ether. The solid residue, containing the morpholine halide salt, was filtered off. The ethereal extract was dried over sodium sulfate. The product obtained after removal of the ether was distilled on an oil bath (in the case of alkylated morpholine derivatives) or vacuum-distilled (in the case of aralkylated derivatives). Morpholine can be regenerated from the residual halide salt by distillation, on heating the salt with solid alkali (calculated in the proportion 0.5 g of KOH to 1 g of salt).

By this means we prepared compounds III, IV and VII-IX, in the yields indicated in Table 1.

Synthesis of 9,10-bis(morpholinomethyl)-anthracene (X). The starting material 9,10-bis(chloromethyl)-anthracene was prepared by chloromethylation of anthracene according to [24].** Purification of the crude product obtained was carried out by a method similar to that of [25] by a twofold suspension of the impure material in dioxan. The residue, insoluble in dioxan, after drying in a vacuum desiccator was recrystallized from hot toluene. The precipitate from the filtrate (hot filtration) was a light-yellow substance of m.p. 281°. The 9,10-bis(chloromethyl)-anthracene obtained was analyzed for chlorine content by oxidation with sodium peroxide and subsequent titration by the Volhard method [26].

Found %: Cl 25.50. $C_{12}H_{12}Cl_2$. Calculated %: Cl 25.60.

9,10-bis(chloromethyl)-anthracene can cause irritation of the mucous membrane of the eyes, swellings of the face and eczema-like irritation of the skin.

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* With the assistance of student B. N. Klopov.

** The experiments on the chloromethylation of anthracene were carried out with the assistance of students O. A. Almazov and S. A. Tikhomirov.

2.7 g of 9,10-bis (chloromethyl)-anthracene and 8.6 g of morpholine were refluxed in an oil bath at 125-130° for 1 hour. The reaction mixture was then left to stand for 24 hours after which it was diluted with water. The precipitate that separated was filtered off and thoroughly washed with water until the aqueous washings were free from Cl^-, then dried in a drying oven (80°). 1.8 g (46.2 %) of a yellow substance of m.p. 190-200° was obtained. In another experiment the crude product melted at 213°. The yellow solid obtained was treated for purification with concentrated hydrochloric acid (about 75 ml), the hydrochloric acid solution was filtered and 9,10-bis (morpholinomethyl)-anthracene was precipitated from the filtrate by sodium hydroxide solution (added until the reaction to litmus was alkaline). The light-yellow precipitate formed was filtered off, washed with water and dried. It could be recrystallized from hot benzene. M.p. 229-230°. 9,10-bis (morpholinomethyl) anthracene is insoluble in water, alcohol and ether, difficultly soluble in acetone and soluble in benzene and glacial acetic acid.

Found %: C 76.27; H 7.59; N 7.13. $C_{22}H_{29}O_2N_2$. Calculated %: C 76.56; H 7.49; N 7.44.

SUMMARY

1. Improved conditions have been found for the preparation of N-alkylated and N-aralkylated morpholine derivatives by condensation of morpholine with alkyl and aralkyl halides. Nine morpholine derivatives have been synthesized in this way, with yields from 45 to 84%.

2. 9,10-bis (morpholinomethyl)-anthracene and sec -n-octylmorpholine, not described in the literature, have been prepared.

3. The densities, refractive indices and viscosities, not recorded in the literature, of some of the compounds prepared, have been determined.

4. Comparison of the constants obtained shows that with increasing length of the aliphatic radical substituting the hydrogen on the nitrogen atom of the morpholine ring, the boiling points of the derivatives increase, the densities decrease and the refractive indices and viscosities increase. The introduction of aromatic rings raises the boiling points, densities, refractive indices and viscosities to an increasing extent with increase in the number of rings.

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THE ENTHALPY OF FORMATION OF COMPOUNDS OF CADMIUM WITH PHOSPHORUS, ARSENIC AND ANTIMONY

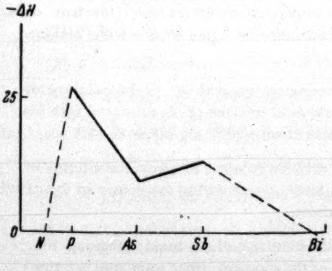
S. A. Shchukarev, M. P. Morozova and M. M. Bortnikova

It was reported earlier that the variation in the heats of formation of the series of compounds of nitrogen, phosphorus, arsenic, antimony and bismuth with zinc, in contrast to that of the heats of formation of the compounds of these elements with magnesium or strontium, is subject to the rule of secondary periodicity [1]. We were interested in examining how the heats of formation of compounds of cadmium with the elements of the main subgroups of Group V behave. If cadmium in fact forms the compound CdN_2 with nitrogen, then it is extremely unstable [2]. With phosphorus it forms the compound Cd_3P_2 and also a phosphide of the probable formula CdP_2, again evidently of poor stability [3].

In the system cadmium-arsenic the existence of the compound Cd_3As_2 has been established [3-5].

The system cadmium-antimony has been studied fairly fully by a number of authors [6-8]. In this system the existence of the compounds CdSb and Cd_3Sb_2 has been established.

Compounds of cadmium with bismuth, at least thermodynamically stable compounds, do not exist.



Variation of enthalpy of formation of compounds of cadmium with the elements of the main subgroup of Group V, with atomic number.

For the synthesis of the compounds, metallic cadmium, purified by distillation in high vacuum, and chemically pure arsenic, antimony and phosphorus, tested by spectrographic analysis, were used.

Cadmium phosphide Cd_3P_2 was prepared by the action of phosphorus on metallic cadmium at 450-500°. The two materials were placed separately in boats in a Pyrex glass tube, which was sealed after thorough evacuation. Excess phosphorus was taken with respect to its content in Cd_3P_2. At the end of the reaction between the cadmium and phosphorus the excess of the latter was distilled off. Cadmium phosphide prepared in this way is a dark-gray crystalline powder. The x-ray spectrograms showed no lines corresponding to the free components.

Cadmium arsenide Cd_3As_2 was prepared in the same way as for cadmium phosphide but at a higher temperature (600-700°). X-ray spectrograms recorded for the preparations obtained in this way did not show lines corresponding to the free components.

We prepared cadmium antimonide by fusing the components together in the stoichiometric ratio. The fusion was carried out in sealed Pyrex glass ampoules at 550-560° for 8-10 hours.

The x-ray spectrogram of the preparation showed a single structure for this material also. The results of analysis of the materials synthesized are given below.

Found %: Cd 84.63, 84.35; P 15.35, 15.43. Cd_3P_2. Calculated %: Cd 84.47; P 15.53.
Found %: Cd 69.45, 69.30; As 30.55, 30.64. Cd_3As_2. Calculated %: Cd 69.20; As 30.80.
Found %: Cd 58.10, 57.85; Sb 41.87, 41.75. Cd_3Sb_2. Calculated %: Cd 58.06, Sb 41.94.

TABLE 1

Enthalpy of Formation (in kcal/g mole)

$3Cd_p + 2P_p = Cd_3P_2$	$3Cd_p + 2As_p = Cd_3As_2$	$3Cd_p + 2Sb_p = Cd_3Sb_2$
−29.5	−11.5	−15.4
−25.4	− 8.9	−13.3
	− 9.5	−12.1
Mean . .−27.4±2.0	−10.0±2.0	−13.9±1.8

TABLE 2

Compound	Heat of formation (kcal)	Compound	Heat of formation (kcal)
ZnO	83.40	CdO	62.4
ZnS	44.3	CdS	34.5
$ZnCl_2$	99.3	$CdCl_2$	93.1
ZnSe	34.0	CdSe	25.0
ZnTe	28.2	CdTe	24.5
Zn_3P_2[12]	98.0	Cd_3P_2	27.4
Zn_3As_2[13]	30.5	Cd_3As_2	10.0
Zn_3Sb_2[14]	48.0	Cd_3Sb_2	13.9

In order to determine the enthalpy of formation of cadmium phosphide, arsenide and antimonide use was made of their reaction with 1 N potassium bromide saturated with bromine, the latter being present in excess.

As we did not know exactly the reaction products of the compounds being investigated and KBr solution saturated with bromine, we determined the heats of reaction of the corresponding elements under the same experimental conditions as for the compounds. For the heat of reaction of cadmium the figure 87.6 + 1 was obtained, for arsenic 103 + 1.0 and for phosphorus 173.6 + 2.0 kcal/g atom.

The calorimetric method has been described previously [9]. The "water-equivalent" of the calorimeter was determined from the heat of reaction of antimony with hydrochloric acid solution (1:4) saturated with bromine, the standard value of the heat of reaction of antimony under these conditions being taken as 91.6 kcal/g atom.

The reaction of cadmium phosphide and arsenide with $KBr-Br_2$ solution resulted in complete solution of the materials; in the case of cadmium antimonide the cadmium went into solution during the course of the calorimetric experiment and the antimony remained in the form of the element.

The enthalpy of formation of the compounds of cadmium with the elements of the main subgroup of Group V was obtained as the difference between the heats of reaction of the elements (that went into solution) with $KBr-Br_2$ solution and the heats of reaction of the compounds with the same solution.

By this means the respective values of the enthalpy of formation (in kcal per gram mole) of the compounds of cadmium with phosphorus, arsenic [illegible]mony, given in Table 1, were found.

The value found by us for Cd_3As_2 is close to that found by Weibke and Kubaschewski [10] (− 14.0 ± 2.5 kcal/g mole). The enthalpy of formation of Cd_3Sb_2 was determined by Bietz and Haase [11]: their figure was 4 kcal/g mole. Our figure seems the more probable, being in good agreement with the high stability of this compound.

From the graph, which shows the variation in enthalpy of formation of compounds of cadmium with the elements of the main subgroup of Group V as a function of the atomic numbers of the latter, it is obvious that the variation in enthalpy of formation in the series $Cd_3N_2-Cd_3Bi$ is subject to the rule of secondary periodicity.

As a rule the heats of formation of zinc compounds exceed those of the analogous cadmium compounds by not more than 35%. The compounds with the elements of the main subgroup of Group V form an exception (Table 2).

The change from zinc to cadmium is accompanied in this case by a sharp reduction (approximately 3-fold) in the heats of formation. This interesting phenomenon is in full accord with the fact that by a further change to mercury – the last element of the secondary subgroup of Group II – further reduction in these values evidently takes place because compounds of mercury with phosphorus, arsenic and antimony cannot generally be prepared.

SUMMARY

1. The values of the enthalpy of formation of Cd_3P_2, Cd_3As_2 and Cd_3Sb_2 have been determined.

2. It is stated that aginst the background of the general closeness of the values of the heats of formation of analogous zinc and cadmium compounds there is a marked difference in the heats of formation of their compounds with the elements of the main subgroup of Group V. The substitution of zinc by cadmium in these compounds is accompanied by a sharp reduction in the heats of formation.

3. The variation in the heats of formation of compounds of cadmium with the elements of the main subgroup of Group V are subject to the rule of secondary periodicity.

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ON THE REACTIONS OF ALKYLDICHLOROSILANES WITH CHLORINATED HYDROCARBONS

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It is stated in the patent literature [1] that methyldichlorosilane reacts with chlorobenzene at 150-300° in the presence of 0.1-5 wt % of $AlCl_3$ or BCl_3 according to the scheme

$$CH_3SiHCl_2 + C_6H_5Cl \rightarrow CH_3(ClC_6H_4)SiCl_2 + H_2.$$

At 450° the reaction between methyldichlorosilane and chlorobenzene does not require a catalyst [2]; however, the main reaction products are methylphenyldichlorosilane and methyltrichlorosilane. In the case of p-dichlorobenzene the isomeric methyl(chlorophenyl)dichlorosilanes are formed together with $CH_3(C_6H_5)SiCl_2$ and CH_3SiCl_3. Evidently at high temperatures, in the absence of catalyst, reactions (I) and (II) occur concurrently,

$$XC_6H_4Cl + CH_3SiHCl_2 - \begin{cases} \nearrow CH_3(XClC_6H_3)SiCl_2 + H_2 & \text{(I)} \\ \searrow CH_3(XC_6H_4)SiCl_2 + HCl, & \text{(II)} \end{cases}$$
$$\text{where } X = H, Cl.$$

The formation of methyltrichlorosilane in these processes evidently arises as a result of the secondary reactions (III) and (IV).

$$CH_3SiHCl_2 + HCl \rightarrow CH_3SiCl_3 + H_2 \qquad \text{(III)}$$
$$CH_3(Cl_2C_6H_3)SiCl_2 + CH_3SiHCl_2 \rightarrow CH_3(ClC_6H_4)SiCl_2 + CH_3SiCl_3 \qquad \text{(IV)}$$

At 525° in the presence of palladium the reaction of methyldichlorosilane with chloro- and trichlorobenzene [3] proceeds in the main according to scheme (II), giving $CH_3(C_6H_5)SiCl_2$ and $CH_3(Cl_2C_6H_3)SiCl_2$ respectively.

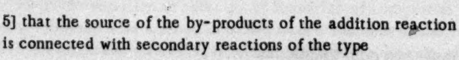
It was shown recently [4, 5] that on reaction of alkylchlorosilanes with alkyl and methallyl chlorides in the presence of 1% of platinum on charcoal at 160° the main effect is the addition

$$CH_2{=}CR'CH_2Cl + RSiHCl_2 \xrightarrow{Pt/C} ClCH_2CHR'CH_2Si(R)Cl_2,$$
$$\text{where } R = CH_3,\ C_2H_5;\ R' = H,\ CH_3.$$

However, in addition to the γ-chloroalkylalkyldichlorosilanes, secondary products are also formed (alkyltrichlorosilanes and dialkyldichlorosilanes).

Under similar conditions the addition of alkyldichlorosilanes to vinyl chloride [6] differs from their reaction with allyl chloride only in the direction of the addition (which in this case, in spite of Markovnikov's rule, leads to the formation of α-chloroethylalkyldichlorosilanes), not differing in principle in the nature of the secondary products. At the same time, according to Weinberg [7] the reaction of organodichlorosilanes (CH_3SiHCl_2, $C_6H_5SiHCl_2$, etc.) with excess vinyl chloride at 600° proceeds according to scheme (II) with the formation of compounds of the type $R(CH_2{=}CH)SiCl_2$.

The supposition [4, 5] that the source of the by-products of the addition reaction between alkyldichlorosilanes and allyl chloride is connected with secondary reactions of the type



$$\underset{\displaystyle R}{Cl_2Si}CH_2\underset{\displaystyle R'}{CH}CH_2Cl + RSiHCl_2 \xrightarrow[t^\circ]{Pt} \underset{\displaystyle R}{Cl_2Si}CH_2\underset{\displaystyle R'}{CH}CH_3 + RSiCl_3,$$

has not obtained experimental confirmation inasmuch as the reaction between γ-chloropropylethyldichlorosilane and ethyldichlorosilane did not lead, under addition-reaction conditions, to the formation of products in which hydrogen was exchanged for chlorine. Hence the formation of alkyltrichlorosilanes and dialkyldichlorosilanes in the reaction of $RSiHCl_2$ with halo-olefins is explained [5] by schemes (V) and (VI)

$$CH_2{=}CH(CH_2)_nCl + RSiHCl_2 \rightarrow CH_2{=}CH(CH_2)_nH + RSiCl_3 \qquad (V)$$

$$CH_2{=}CH(CH_2)_nH + RSiHCl_2 \rightarrow CH_3(CH_2)_{n+1}Si(R)Cl_2, \qquad (VI)$$

where $R = CH_3$, C_2H_5, $n = 0 + 1$.

In view of the above considerations it was of definite interest to investigate the possibility of the reaction of scheme (V), which up to the present time has not been substantiated experimentally. With this objective we studied the reaction of ethyldichlorosilane with n-propyl, isopropyl and allyl chlorides.*

We have shown previously [8] that these chlorinated hydrocarbons in the presence of anhydrous aluminum chloride, even in the cold, readily undergo with triethylsilane an exothermic reaction of combined hydrogenation–halogenation; in this reaction the reaction rate and yield of triethylchlorosilane are determined mainly by the lability of the chlorine atom in the chlorinated hydrocarbon, in accordance with the series $C_3H_5Cl >$ iso-$C_3H_7Cl >$ $>$ n-C_3H_7Cl. In comparison with R_3SiH, the Si–H bond in $RSiHCl_2$ is less polarized $(\overset{\delta+}{Si}-\overset{\delta-}{H})$, which is reflected, for example, in its higher frequency in vibrational spectra and in its lower tendency towards heterolytic reactions.** The I-effect of the chlorine atoms decreases the hydride character of the hydrogen atom attached to silicon, deactivates the Si–H bond in $RSiHCl_2$ and, correspondingly, the exchange reaction between hydrogen and halogen. This is shown, in particular, by the fact that the reaction investigated by us

$$C_2H_5SiHCl_2 + RCl \xrightarrow{AlCl_3} C_2H_5SiCl_3 + RH, \qquad (VII)$$

where $R = C_3H_5$, iso-, n-C_3H_7,

in the presence of 2-4 moles % of anhydrous aluminum chloride takes place extremely slowly at room temperature; it proceeds at a satisfactory rate only on heating the reaction mixture to 50-60°.***

From the data in the table it can be seen that in the case of isopropyl chloride in which the chlorine atom is more labile than in n-C_3H_7Cl, the conversion of ethyldichlorosilane to ethyltrichlorosilane is correspondingly higher. However, in the aliphatic series it is the reactivity of the Si–H bond that is the determining factor for reaction (VII) and not of the C–Cl bond. This is clearly indicated by the example of the reaction of ethyldichlorosilane with allyl chloride: as a result of the low activity of the Si–H bond in $C_2H_5SiHCl_2$ with respect to the hydrogen-chlorine exchange reaction, a secondary process predominates here – resin formation resulting from polymerization of the original allyl chloride and also of the propylene formed by the action of $AlCl_3$, while only a third of the ethyldichlorosilane is converted to ethyltrichlorosilane.

It is important to note that in contrast to R_3SiH [8] the reaction of ethyldichlorosilane with RCl which takes place on addition of the chlorinated hydrocarbon to a mixture of ethyldichlorosilane and $AlCl_3$ does not occur with the reverse procedure – addition of $C_2H_5SiHCl_2$ to a mixture of RCl and $AlCl_3$. The introduction of isopropyl chloride to a mixture of ethyldichlorosilane and aluminum chloride at room temperature does not give rise to any noticeable reaction; this begins only on heating the reaction mixture. At the same time, addition of n-C_3H_7Cl to a mixture of $C_2H_5SiHCl_2$ and $AlCl_3$, that has first been heated to boiling and then cooled to room temperature, gives rise to a slow exchange reaction.

Hence from an examination of the question of the scheme (VII) reaction mechanism it may be considered that a labile complex of ethyldichlorosilane and aluminum chloride is formed initially****

$$C_2H_5SiHCl_2 + AlCl_3 \rightarrow [C_2H_5SiHCl]^+ [AlCl_4]^-,$$

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* It is known [4] that on addition of ethyldichlorosilane to allyl chloride the secondary products – $RSiCl_3$ and R_2SiCl_2 are formed in greatest quantity.

** This same fact results in a considerably higher reactivity of $RSiHCl_2$ and $HSiCl_3$ in comparison with R_3SiH in homolytic reactions of the S–H bonds. There are also other views on this question [9].

*** In this connection it should be noted that although triethylsilane reduces n-butyltrichlorosilane in the presence of aluminum chloride, ethyldichlorosilane does not react under similar conditions [10].

**** Investigation of the kinetics of disproportionation of the methylchlorosilanes in the presence of aluminum chloride has shown that in the reaction mixture the $AlCl_3$ occurs almost entirely in the form of complexes with the chlorosilanes [11].

Reaction of Ethyldichlorosilane with Chlorinated Hydrocarbons in the Presence of Aluminum Chloride

RCl	Molar ratio of C_2H_5-HCl_2 and RCl	Quantity of $AlCl_3$ (in moles % on $C_2H_5SiHCl_2$	Conversion of $C_2H_5SiHCl_2$ to $C_2H_5SiCl_3$ (in %)	Yield (in %, calculated on the ethyldichlorosilane reacted)
C_3H_5Cl	1:1	4.0	32.5	73.8
iso-C_3H_7Cl	1:1.6	3.0	66.2	90.2
n-C_3H_7Cl	1:1	2.0	62.7	90.5

bringing about the conversion of ethyldichlorosilane to ethylchlorosilane

$$C_2H_5SiHCl_2 + [C_2H_5SiHCl]^+[AlCl_4]^- \rightleftarrows [C_2H_5SiCl_2]^+[AlCl_4]^- + C_2H_5SiH_2Cl.$$

The halogenated hydrocarbons form more stable complexes with aluminum chloride [12, 13] that can favor the reaction

$$RCl + [C_2H_5SiCl_2]^+[AlCl_4]^- \rightarrow [R]^+[AlCl_4]^- + RSiCl_3$$

The $[R]^+[AlCl_4]^-$ complex evidently cannot be reduced by ethyldichlorosilane in which the hydride character of the Si—H bond is weak. In ethylchlorosilane, however, the Si—H bond is evidently sufficiently active to reduce the complex.

$$C_2H_5SiH_2Cl + [R]^+[AlCl_4]^- \rightarrow [C_2H_5SiHCl]^+[AlCl_4]^- + RH, \text{ etc.}$$

The proposed reaction mechanism scheme explains satisfactorily the fact that there is no reaction on adding $RSiHCl_2$ to a mixture of alkyl chloride and aluminum chloride in which the latter occurs in the form of the comparatively stable complex $[R]^+[AlCl_4]^-$.

EXPERIMENTAL

The ethyldichlorosilane was a product of b.p. 74.5-75.5°, prepared by fractionation of a technical mixture of ethylchlorosilanes through a glass column with a ceramic packing (efficiency, 40 theoretical plates). The organic halogenated derivatives were pure commercial preparations. The aluminum chloride was an anhydrous, purified material.

The experiments were carried out in an apparatus consisting of a three-necked flask fitted with a thermometer, dropping funnel and reflux condenser connected through a calcium chloride tube to a gasometer.

Reaction of Ethyldichlorosilane with Chlorinated Hydrocarbons

1. 15.7 g of iso-C_3H_7Cl was added over 20 minutes to a mixture of 25.8 g of ethyldichlorosilane and 0.53 g of $AlCl_3$. No reaction was observed at room temperature. Heating of the reaction mixture brought about a vigorous reaction accompanied by evolution of gas and exothermic heating of the mixture to 60°. On heating the mixture further a constant boiling point (91°) was rapidly established. On distilling the mixture 8.7 g of unreacted ethyldichlorosilane (33.7% of the original) and 19.5 g of ethyltrichlorosilane (90.2% calculated on the ethyldichlorosilane reacted) were obtained. The residue in the flask was a black, viscous resin. 2.1 liters of propane was collected during the course of the reaction.

2. A mixture of 19.5 g of ethyldichlorosilane and 0.6 g of $AlCl_3$ was heated to boiling and then cooled to room temperature. On addition of n-propyl chloride a slow reaction began, accompanied by evolution of gas. On heating the mixture to 60° the reaction proceeded vigorously. After 140 minutes of moderate heating the temperature of the reaction mixture reached 91° after which the reaction practically came to an end and further

addition of n-propyl chloride resulted only in lowering the boiling point of the mixture to 68.5°, and the evolution of gas practically ceased (2.6 liters of propane was collected). In all 18.6 g of n-propyl chloride was added, i.e., 150% of the necessary calculated quantity. On distillation of the reaction products 6.4 g of unreacted ethyldichlorosilane (37.3% of the original) and 14.0 g of ethyltrichlorosilane (90.5%) were obtained. The residue in the flask (1.5 g) was a black, viscous resin that solidified in the air.

3. After adding 19.4 g of ethyldichlorosilane, over a period of half an hour, to a boiling mixture of n-propyl chloride (23.5 g) and aluminum chloride (0.6 g) a constant boiling point of the mixture (49°) was established but no evolution of gas was observed. Further heating of the mixture for 1 hour brought about only resinification resulting evidently from secondary reactions of the alkyl halide with aluminum chloride. On distilling the reaction mixture the initial materials were obtained.

4. 15.3 g of allyl chloride was added over 90 minutes, with slight heating, to a mixture of 25.8 g of ethyldichlorosilane and 1.07 g of $AlCl_3$, bringing about no noticeable reaction. The mixture was refluxed for a further 90 minutes and this led to a slow evolution of gas, rapid establishment of a constant boiling point (76°) and appreciable resinification of the mixture. On distilling the reaction products 2.25 g of unreacted allyl chloride, 17.4 g of unreacted ethyldichlorosilane (67.5% of the original) and 7.85 g of ethyltrichlorosilane (73.8% of the ethyldichlorosilane reacted) were obtained. The residue in the flask (7.4 g) was a viscous, black resin with an odor of naphtha (petroleum), becoming brittle in the air. The gas collected during the experiment, which amounted to 0.5 liter, was entirely absorbed by bromine (propylene).

The ethyltrichlorosilane obtained from the reactions between ethyldichlorosilane and chlorinated hydrocarbons had practically the same constants in all the experiments. After a second distillation it had the following constants.

B.p. 98.2°, n_D^{20} 1.4253, d_4^{20} 1.2393, MR_D 33.76; calc. 33.78.
Found %: Cl 65.0, 65.2; Si 17.3. $C_2H_5SiCl_3$. Calculated %: Cl 65.05; Si 17.17.

SUMMARY

It is shown that in the presence of aluminum chloride ethyldichlorosilane takes part in a combined hydrogenation – halogenation reaction with chlorinated aliphatic hydrocarbons, reducing the latter to the corresponding hydrocarbons and being converted in the process to ethyltrichlorosilane.

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POLAROGRAPHY OF THE THERMAL DECOMPOSITION OF 2,2'-AZOBISISOBUTYRONITRILE IN VINYL BUTYL ETHER AND METHYL METHACRYLATE

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A number of works [1-7] are devoted to the decomposition of aliphatic azo compounds which are initiators of radical polymerization.

Most of the authors judged the rate of decomposition of the azo compounds investigated by the amount of nitrogen evolved. Bawn and Mellish [5] carried out the decomposition of the azo compound in a medium of brightly colored diphenyl-β-picrylhydrazyl free radicals which formed stable compounds with the radicals of the azo compound. The reaction was accompanied by a sharp change in the color of the solution. The cited authors checked the course of decomposition of the azo compound by a colorimetric method. Bevington, Bradbury and Burnett [7] used an isotopic indicator method for this purpose.

It was of interest also to use a polarographic method for study of the course of decomposition of azo compounds, 2,2'-azobisisobutyronitrile (ABN), in particular. Besides the direct determination of the decomposing azo compound at any stage of polymerization, we had in mind the possibility of simultaneously determining, firstly, nitriles [8] as deactivation products of azo-compound radicals, and secondly, the monomer in which the decomposition of the initiator takes place. Polarographic data thus obtained may also characterize the state of oxidation-reduction of the investigated medium during the polymerization process.

We carried out the decomposition of ABN in two media which sharply differed in their tendency toward polymer-chain formation. As a substance only slightly susceptible to radical polymerization with the initiator named, vinyl butyl ether was chosen; in contrast to this, as a substance which polymerizes intensely under similar conditions, methyl methacrylate was selected.

EXPERIMENTAL

The ABN used in the work was twice-recrystallized from purified methyl alcohol and had m.p. 101°; the methyl methacrylate was distilled beforehand, and the 100-101° fraction was used.

In the case of polymerization in solution 1 ml of a 0.5% solution of ABN in methyl methacrylate was mixed with an equal volume of a solvent consisting of a mixture of benzene and methyl alcohol (1:1) and placed in thin-walled, glass ampules. The sealed ampules were immersed in a water bath in which the temperature was automatically maintained at 60° with an accuracy of ± 0.1°. At half-hour intervals the ampules were taken out of the bath and crushed in a porcelain vessel containing a supporting electrolyte (2 ml of an aqueous solution of $(C_2H_5)_4NI$ + 2 ml of ethyl alcohol). The solution obtained was poured into an electrolyzer and polarographed in order to determine its ABN content. After 100-fold dilution of this solution with supporting electrolyte, the methyl methacrylate content was determined polarographically.

In the case of mass polymerization a 0.1-0.5% solution of ABN in methyl methacrylate or vinyl butyl ether was poured into thin-walled glass ampules in amounts of about 1 g. The sealed ampules were kept at 60° in a water bath. After definite time intervals an ampule containing the solution being investigated was taken out of the water bath and put into a porcelain vessel containing 3 ml of ethyl alcohol. The ampule was crushed with a glass rod, and the contents of the vessel were thoroughly stirred. The alcoholic solution of ABN thus obtained was mixed with an equal volume of supporting electrolyte and put into the electrolyzer for polarographing.

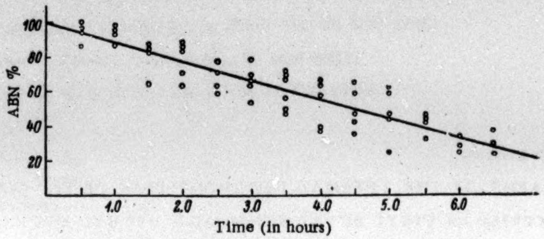

Fig. 1. Variation of quantities of 2,2'-azobisisobutyronitrile (ABN) in a solution of methyl methacrylate, benzene, and methyl alcohol (catalyst content 0.5% with respect to monomer).

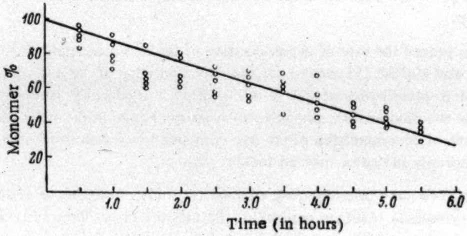

Fig. 2. Variation of quantities of methyl methacrylate on polymerization in a solution of benzene and methyl alcohol (catalyst content 0.5% with respect to monomer).

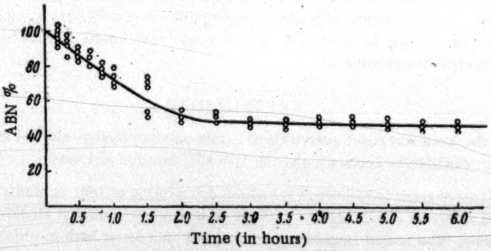

Fig. 3. Variation of quantities of 2,2'-azobisisobutyronitrile (ABN) en bloc with methyl methacrylate (catalyst content 0.5% with respect to monomer).

On polymerization of the methyl methacrylate under the conditions stated above, samples heated more than 2 hours had the form of a continuous, solidified, transparent mass. To extract ABN from solidified samples, the latter were pulverized in a special apparatus constructed by us for pulverizing polymer samples and, at the same time, extracting the unused initiator and monomer from them [9]. The alcoholic extract obtained was freed from fine particles of polymer, mixed with an equal volume of supporting electrolyte, and polarographed to determine ABN. To determine the amounts of methyl methacrylate not polymerized, we put 0.1-0.2 ml of the alcoholic extract into 5 ml of supporting electrolyte and again polarographed.

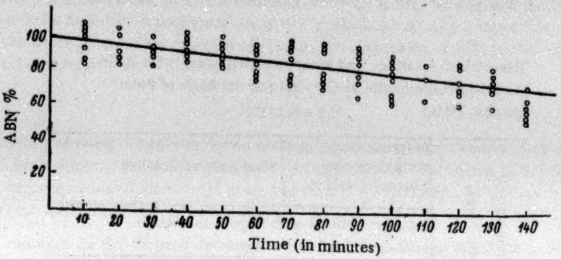

Fig. 4. Variation of quantities of 2,2'-azobisisobutyronitrile (ABN) en bloc with methyl methacrylate (catalyst content 0.1% with respect to monomer).

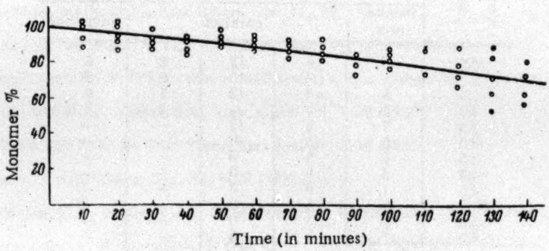

Fig. 5. Variation of quantities of methyl methacrylate on mass polymerization (catalyst content 0.1% with respect to monomer).

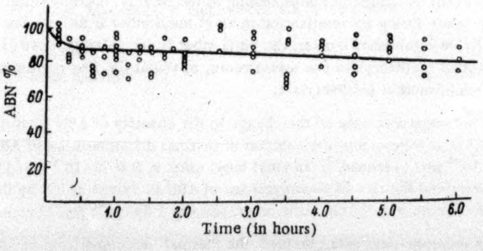

Fig. 6. Variation of quantities of 2,2'-azobisisobutyronitrile (ABN) en bloc with vinyl butyl ether (catalyst content 0.5% with respect to monomer).

The polarography was done by means of a Gor'kii M-7 polarograph with a mirror galvanometer, the current sensitivity of which was I = 150 mm/μa. The measurements were made with a 1 : 10 shunt. The capillary was cylindrical and had a dropping period t = 3 sec and a drop weight m = 0.34 mg; the capillary constant $m^{2/3} \cdot t^{1/6}$ = = 1.83 $mg^{2/3}$ $second^{-1/2}$ at 2.1 v. The height of rise of the mercury bulb provided for a possible decrease of tangential movements [10]. As supporting electrolytes, 50% aqueous-alcoholic solutions of $(C_2H_5)_4NI$ and LiCl were used.

On the basis of multiple measurements of the limiting diffusion currents due to reduction at the mercury drop of the ABN in initial samples and in samples corresponding to definite time intervals, the table and Figs. 1-6 were compiled. The change in the quantities of ABN during polymerization in vinyl butyl ether and methyl methacrylate, as well as the change in the amounts of monomer, may be estimated from these data.

Kinetics of Solution- and Mass Polymerization with 2,2'-Azobisisobutyronitrile as Catalyst (on the Basis of Polarographic Data)

Time from beginning of experiment (in hours)	Polymerization in methyl alcohol-benzene solution (1:1)		Mass polymerization		
	catalyst content with respect to methyl methacrylate (in %)				
	0.5		0.5		0.1
	decrease per 0.5 hour (in % of the initial quantity)				
	monomer	catalyst			monomer
0.5	6	6	12	8	6
1.0	8	7	16	5	5
1.5	5	6	12	5	6
2.0	5	5	—	4	5
2.5	7	5	10	—	—
3.0	5	5	0	—	—
3.5	6	5	0	—	—
4.0	6	5	0	—	—
4.5	7	6	0	—	—
5.0	5	5	0	—	—
5.5	5	5	0	—	—
6.0	7	5	0	—	—

DISCUSSION OF RESULTS

From consideration of the polarograms corresponding to the thermal decomposition of ABN and the subsequent consumption of the latter during polymerization in vinyl butyl ether it follows that in this case only reduction of ABN occurs. As we established earlier, the vinyl ether is not polarographed [11]. In the case of decomposition of ABN in methyl methacrylate two waves occur, of which the first corresponds to reduction of ABN and the second to reduction of methyl methacrylate.

From the obtained polarographic data on the change in the quantity of ABN when the content of the latter in the initial sample is 0.5%, it follows that the constant of thermal decomposition of ABN in a methyl methacrylate medium is $0.82 \cdot 10^{-4}$ (m/l) second^{-1}; in vinyl butyl ether it is $0.70 \cdot 10^{-4}$ (m/l) second^{-1}. Lewis and Matheson [1, 2], who determined the rate of decomposition of ABN in xylene at 80° by the quantity of nitrogen evolved, found a value for the constant of the same order, namely $1.53 \cdot 10^{-4}$ (m/l) second^{-1}.

As follows from the polarographic data obtained, the thermal decomposition of ABN is a first-order reaction. During the time interval under investigation (5-6 hours) the dependence of the methyl methacrylate content on time also is linear in character.

On solution polymerization (under the chosen experimental conditions) the change of viscosity with time is negligible, and the catalyst content, determined polarographically, changes uniformly in the course of the polymerization process during the entire period of time investigated. On mass polymerization the viscosity of the sample changes sharply in the course of time. For instance, in the case where the catalyst content is 0.5%, the sample hardens within 2.5 hours, and the change of catalyst content for each 0.5 hour, with respect to its initial value, during subsequent half-hour intervals is equal to zero.

On mass polymerization in vinyl butyl ether the ABN content becomes constant in the first 0.5 hour. On decomposition of the named initiator en bloc with methyl methacrylate, the ABN content becomes stable in 2.5 hours. When subsequent samples are polarographed, no change in ABN content is observed.

The rates of decrease of the quantity of ABN in methyl methacrylate, when the concentration of the former is 0.1%, is considerably less than those for a concentration of 0.5%. It may be supposed that, in view of the lower rate of polymerization for an initiator concentration of 0.1%, which means also a lower rate of consumption of initiator radicals, the equilibrium of the reaction of thermal decomposition of ABN in this case is displaced to a lesser extent in the direction of radical formation.

SUMMARY

1. The possibility of using the polarographic method for the study of the course of the process of radical polymerization has been shown. The conditions for the polarographic determination of 2,2'-azobisisobutyronitrile on thermal decomposition of vinyl butyl ether and methyl methacrylate, as well as the simultaneous determination of methyl methacrylate, have been found.

2. The rate constant for the thermal decomposition of 2,2'-azobisisobutyronitrile in the named media has been determined by the polarographic method.

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PREPARATION OF CERTAIN COMPOUNDS WITH TWO ISOPROPENYL GROUPS

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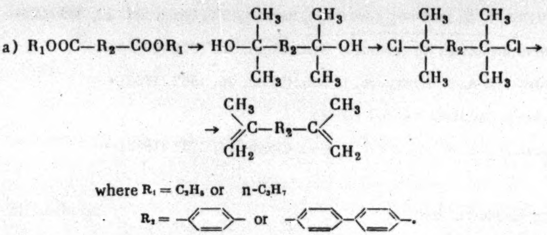
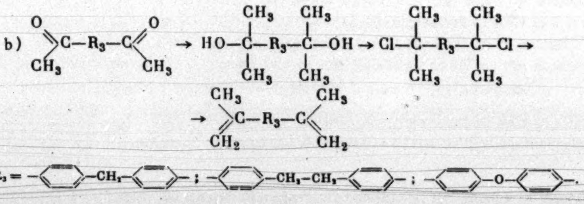
Compounds containing two isopropenyl groups are of interest in connection with the development of a new method of polymer preparation [1]. However, there are practically no data in the literature, either on methods of synthesis or on the properties of these compounds. Only a method for the synthesis of p-diisopropenylbenzene is described [2], but this method is inconvenient for the preparation of appreciable quantities of product. Therefore a new, more efficient method of preparation of p-diisopropenylbenzene is proposed by us. As regards 4,4'-diisopropenylbiphenyl, 4,4'-diisopropenyldiphenylmethane, 4,4'-diisopropenyldiphenylethane, and 4,4'-diisopropenyldiphenyl ether, they are wholly unknown in the literature. True, 4,4'-diisopropenylbiphenyl is mentioned in the cited work [3], but apparently the authors were unable to obtain it in sufficiently pure form.

The over-all scheme of preparation of the final unsaturated compounds synthesized by us is as follows:



$$a)\ R_1OOC{-}R_2{-}COOR_1 \rightarrow HO{-}\overset{CH_3}{\underset{CH_3}{C}}{-}R_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OH \rightarrow Cl{-}\overset{CH_3}{\underset{CH_3}{C}}{-}R_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}Cl \rightarrow \overset{CH_3}{\underset{CH_2}{>}}C{-}R_2{-}C\overset{CH_3}{\underset{CH_2}{<}}$$

where $R_1 = C_2H_5$ or n-C_3H_7



$$b)\ \overset{O}{\underset{CH_3}{>}}C{-}R_3{-}C\overset{O}{\underset{CH_3}{<}} \rightarrow HO{-}\overset{CH_3}{\underset{CH_3}{C}}{-}R_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OH \rightarrow Cl{-}\overset{CH_3}{\underset{CH_3}{C}}{-}R_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}Cl \rightarrow \overset{CH_3}{\underset{CH_2}{>}}C{-}R_3{-}C\overset{CH_3}{\underset{CH_2}{<}}$$

We rejected the direct dehydration of diols (by means of such catalysts as $KHSO_4$, Al_2O_3, etc), which gives insignificant yields, and used a two-step method of preparation of unsaturated compounds through the corresponding dichlorides with subsequent splitting off of hydrogen chloride. Both steps – conversion to the chloride and splitting off of the hydrogen chloride – proceed with good yields (90-95%).

The synthesis according to scheme "a" was carried out in the case where the corresponding diketones were difficultly soluble or difficult to prepare. Such are p-diacetylbenzene and 4,4'-diacetylbiphenyl. Instead of diketones, therefore, it is more expedient to use the corresponding dicarboxylic acid esters, the solubility of which can be regulated by selecting the proper alkoxy groups. Carrying out the reaction of diacetyl derivatives or dicarboxylic acid esters with methylmagnesium bromide presents no difficulties; the diols are obtained in good yield. Replacement of the hydroxyl group by a chlorine atom also proceeds smoothly. As a rule, the chlorides obtained are unstable compounds and readily split off hydrogen chloride even on standing.

The final products – diisopropenyl derivatives of benzene, biphenyl, diphenylmethane, etc.– are colorless, well-crystallized substances, stable on keeping for a short time.

On prolonged storage they may spontaneously polymerize to an insoluble, porous mass.

The structures, elementary analyses, and melting points of the substances obtained are given in the table.

The author thanks M. M. Koton, in whose laboratory the work was done, for valuable advice and interest in the work.

EXPERIMENTAL

1. Preparation of 1,4-diisopropenylbenzene (III). The starting material is diethyl terephthalate, which is much more soluble in ether and benzene than dimethyl terephthalate. To the Grignard reagent prepared from 20 g of magnesium and 95 g of methyl bromide was added dropwise a solution of 44.4 g of diethyl terephthalate in anhydrous benzene. After this the mixture was warmed for 1 hour in a water bath and then poured into a mixture of 400-500 g of ice and 200 g of ammonium chloride. The solvent was evaporated and the precipitated crystals were separated out, washed with water, dried, and recrystallized from benzene. Yield of pure 1,4-bis(α-hydroxyisopropyl)benzene (I), 24-25 g (66%).

Thirty g of substance (I) and 150 ml of benzene were put into a water-cooled Erlenmeyer flask and a current of dry hydrogen chloride passed into the mixture until the solid matter dissolved. The resulting solution of 1,4-bis(α-chloroisopropyl)benzene (II) was washed with water and 10% soda solution and dried with anhydrous calcium chloride. The solvent was distilled off in vacuo (without heating) or evaporated. The precipitated crystals were dissolved in petroleum ether. On cooling the solution to (– 30)-(– 40)° fine crystals precipitated, which were immediately separated out, washed with a small amount of cooled petroleum ether, and dried in air. (However, recrystallization of the dichloride is not necessary for the next operation).

To prepare 1,4-diisopropenylbenzene the dichloride (II) was dissolved in 100 ml of pyridine and the solution boiled for 15 minutes. The mixture was poured into 0.5 l of cold water. The resulting precipitate was separated out and washed several times with water. The diisopropenylbenzene (III) formed was steam distilled and then recrystallized from alcohol, a small amount of activated charcoal being added. Yield of pure product, 18 g (75%, calculated on the basis of substance (I)).

2. Preparation of 4,4'-diisopropenylbiphenyl (VI). The starting material was propyl 4,4'-biphenyldicarboxylate (XV), m.p. 75°, prepared from 4,4'-biphenyldicarbonyl chloride and propyl alcohol. To prepare 4,4'-bis(α-hydroxyisopropyl)biphenyl (IV), 3.3 g of ester (XV), 1 g of magnesium, and 4 g of methyl bromide were used. The reaction was carried out similarly to the preparation of compound (I). The obtained (IV) was recrystallized from aqueous methyl alcohol. Yield, 18 g (65%).

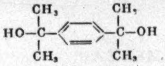
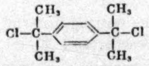
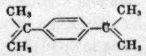
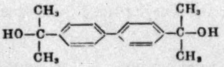
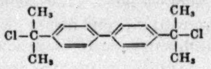
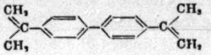
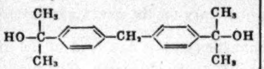
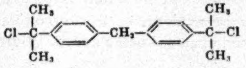
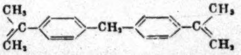
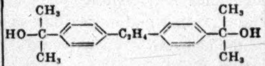
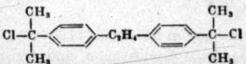
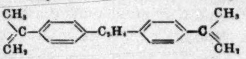
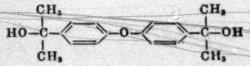
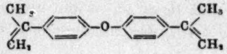
4,4'-Bis(α-chloroisopropyl)biphenyl (V) was obtained in nearly quantitative yield by passing dry hydrogen chloride into a suspension of (IV) in benzene, recrystallized from hexane, and converted by heating with pyridine to 4,4'-diisopropenylbiphenyl (VI), which was crystallized from ethyl alcohol. Fine, shiny platelets, soluble in benzene, difficultly soluble in acetone and alcohols. Yield, 1 g (68%, calculated on the basis of substance (IV)).

3. Preparation of 4,4'-diisopropenyldiphenylmethane (IX). The starting material was 4,4'-diacetyldiphenylmethane (XVI), m.p. 92° (literature data: 93° [4]), 12.6 g of which was brought into reaction with the Grignard reagent prepared from 3 g of magnesium and 12 g of methyl bromide. 4,4'-Bis(α-hydroxyisopropyl)diphenylmethane (VII) was obtained in the form of a viscous liquid which split off water on distillation; therefore the product (VII) was converted without purification to 4,4'-bis(α-chloroisopropyl)diphenylmethane (VIII).

To split off hydrogen chloride, the obtained dichloride (VIII) was boiled with pyridine. The reaction product was recrystallized from ethyl alcohol, a little activated charcoal being added. Yield of substance (IX), 4.5 g (36%, calculated on the basis of substance (XVI)). Shiny leaflets, soluble in benzene and in carbon tetrachloride, difficultly soluble in alcohol.

4. Preparation of 4,4'-diisopropenyldiphenylethane (XII). The starting material was 4,4'-diacetyldiphenylethane (XVII), m.p. 167° (literature data: 168° [5]).

TABLE

Compound		Melting point	Calculated %			Found %		
			C	H	Cl	C	H	Cl
1,4-Bis (α-hydroxyisopropyl)benzene (I)		140° (1424)**	—	—	—	—	—	—
1,4-Bis(α-chloroisopropyl)benzene (II)*		68–69 Dec.	62.34	6.93	30.73	62.67	6.95	30.77
1,4-Diisopropenylbenzene (III)		64.5 (64)**	91.14	8.86	—	91.22	8.81	—
4,4'-Bis(α-hydroxyisopropyl)biphenyl (IV)*		161	80.00	8.15	—	80.04	8.38	—
4,4'-Bis(α-chloroisopropyl)biphenyl (V)*		114	70.35	6.51	23.13	70.48	6.66	23.00
4,4'-Diisopropenylbiphenyl (VI)		183	92.31	7.69	—	92.28	7.78	—
4,4'-Bis(α-hydroxyisopropyl)diphenylmethane VII*		Viscous liquid; splits off water on distillation						
4,4'-Bis (α-chloroisopropyl(diphenylmethane (VIII)*		Unstable liquid; readily splits off HCl						
4,4'-Diisopropenyldiphenylmethane IX)*		57	91.93	8.07	—	91.67	8.08	—
4,4'-Bis(α-hydroxyisopropyl)diphenylethane (X)*		150	80.53	8.72	—	80.43	8.73	—
4,4'-Bis(α-chloroisopropyl)diphenylethane (XI)*		119.5	71.64	7.16	21.19	71.21	7.70	21.24
4,4'-Diisopropenylethane (XII)*		124.5	91.60	8.40	—	91.49	8.40	—
4,4'-Bis(α-hydroxyisopropyl)diphenyl ether (XIII)*		Viscous liquid; readily splits off water on distillation						
4,4'-Diisopropenyldiphenyl ether (XIV)*		107.5	86.40	7.20	—	86.30	7.26	—

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*Compounds marked with an asterisk were obtained for the first time.

**According to literature data [2].

4,4'-Bis(α-hydroxyisopropyl)diphenylethane (X) was prepared in the following manner: 14 g of diketone (XVII), 3 g of magnesium, 50 g of anhydrous benzene, and 25 ml of absolute ether were put into a round-bottom flask provided with stirrer, reflux condenser, and dropping funnel. A solution of 12 g of methyl bromide in 75 ml of absolute ether was added dropwise to the mixture. It was sometimes necessary, for activation, to add a few drops of methylmagnesium bromide solution. At the end of the reaction the mixture was heated for 1 hour more; it was then decomposed by a mixture of ice and ammonium chloride. The resulting substance (X) was recrystallized from benzene. Fine needles readily soluble in alcohols, difficultly soluble in benzene or ether. Yield, 10 g (64%).

4,4'-Bis(α-chloroisopropyl)diphenylethane (XI) was synthesized from 10 g of (X) by the method given above. It was recrystallized from hexane. Fine platelets, quite stable at room temperature. Readily soluble in almost all solvents. Yield, 9 g (82%).

4,4'-Diisopropenyldiphenylethane (XII) was prepared by heating dichloride (XI) with pyridine, as stated above. The product obtained was co-distilled with ethylene glycol and recrystallized from alcohol. Yield of pure product, 3.4 g (50%). Hydrocarbon (XII) is soluble in benzene and carbon tetrachloride, difficultly soluble in petroleum ether and acetone, and poorly soluble in alcohols.

5. Preparation of 4,4'-diisopropenyldiphenyl ether (XIV). The starting material was 4,4'-diacetyldiphenyl ether, m.p. 100° (literature data: 100-101° [6]), 62 g of which was brought into reaction with the Grignard reagent prepared from 12 g of magnesium and 50 g of methyl bromide. 4,4'-Bis(α-hydroxyisopropyl)diphenyl ether (XIII) was obtained in the form of a viscous liquid, which was placed in a distilling flask and heated at 100-140° (10 mm) until the evolution of water ceased. The residue was distilled in vacuo, and the 195-205° fraction (2 mm) was collected. The obtained substance (XIV) was recrystallized from alcohol. Shiny platelets, soluble in benzene and acetone, difficultly soluble in alcohol. Yield, 40 g (65%).

SUMMARY

1. A synthesis of 4,4'-diisopropenylbiphenyl, 4,4'-diisopropenyldiphenylmethane, 4,4'-diisopropenyldiphenylethane, and 4,4'-diisopropenyldiphenyl ether has been worked out.

2. The following compounds have been prepared and described for the first time: 1,4-bis(α-chloroisopropyl)benzene, 4,4'-bis(α-hydroxyisopropyl)biphenyl, 4,4'-bis(α-chloroisopropyl)biphenyl, 4,4'-bis(α-hydroxyisopropyl)diphenylmethane, 4,4'-bis(α-chloroisopropyl)diphenylmethane, 4,4'-diisopropenyldiphenylmethane, 4,4'-bis(α-hydroxyisopropyl)diphenylethane, 4,4'-bis(α-chloroisopropyl)diphenylethane, 4,4'-diisopropenyldiphenylethane, 4,4'-bis(α-hydroxyisopropyl)diphenyl ether, and 4,4'-diisopropenyldiphenyl ether.

3. The method of preparation of p-diisopropenylbenzene has been improved.

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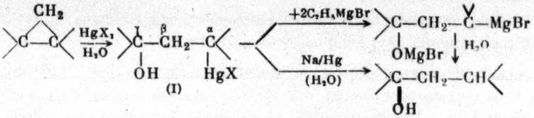
INTERACTION OF CYCLOPROPANE HYDROCARBONS WITH MERCURIC SALTS

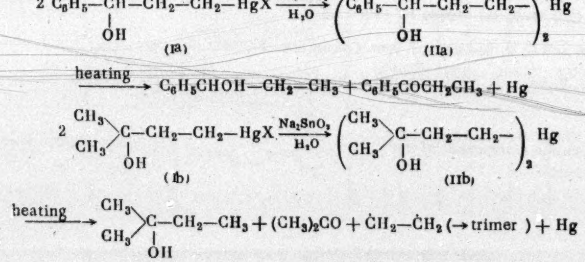
VIII. REACTION OF γ-MERCURATED ALCOHOLS WITH ZINC DUST

R. Ia. Levina and V. N. Kostin

In our earlier papers the reaction of alkyl- and arylcyclopropanes with mercury salts in aqueous solution [1-6], taking place with cleavage of the three-membered ring and leading to the formation of γ-mercurated alcohols (I), was described; the structure of the latter (and hence the position of ring cleavage) was established by their reduction (through replacement of the HgX group by hydrogen) and identification of the alcohols obtained thereby. The reduction of the γ-mercurated alcohols was carried out by treatment with sodium amalgam [1-4] or ethylmagnesium bromide [5, 6].



In order to avoid working with a large quantity of mercury (on reduction with sodium amalgam) or with diethylmercury (produced on reduction with ethylmagnesium bromide), we used another route for proof of the structure of γ-mercurated alcohols (Ia and Ib), which consisted in their symmetrization and the further decomposition of the resulting fully substituted organomercury compounds (IIa and IIb) containing alcohol groups in the γ-position relative to the mercury atom [7]. It was established that if the alcohol groups are secondary (IIa), thermal decomposition leads to the formation of an alcohol and a ketone, both having the carbon skeleton of the original fully substituted organomercury compound; if the alcohol groups in the γ-mercurated alcohol are tertiary (IIb), an alcohol with the same carbon skeleton is formed on thermal decomposition, while a ketone is also formed, owing to cleavage of the carbon-carbon bond; for instance:



$$2\,C_6H_5{-}\underset{OH}{\underset{|}{CH}}{-}CH_2{-}CH_2{-}HgX \xrightarrow[H_2O]{Na_2SnO_2} \left(C_6H_5{-}\underset{OH}{\underset{|}{CH}}{-}CH_2{-}CH_2{-}\right)_2Hg$$

(Ia) (IIa)

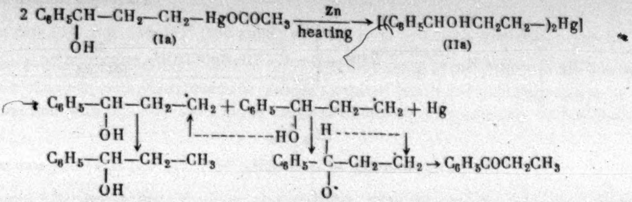
$$\xrightarrow{\text{heating}} C_6H_5CHOH{-}CH_2{-}CH_3 + C_6H_5COCH_2CH_3 + Hg$$

$$2\,(CH_3)_2\underset{OH}{\underset{|}{C}}{-}CH_2{-}CH_2{-}HgX \xrightarrow[H_2O]{Na_2SnO_2} \left((CH_3)_2\underset{OH}{\underset{|}{C}}{-}CH_2{-}CH_2{-}\right)_2Hg$$

(Ib) (IIb)

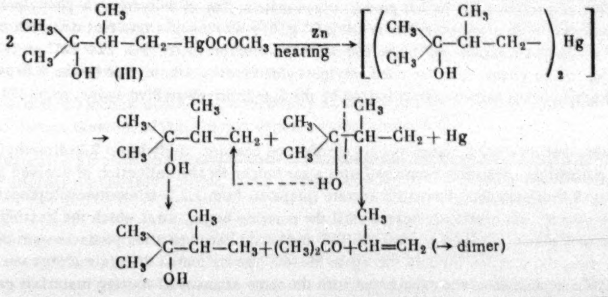
$$\xrightarrow{\text{heating}} (CH_3)_2\underset{OH}{\underset{|}{C}}{-}CH_2{-}CH_3 + (CH_3)_2CO + \dot{C}H_2{-}\dot{C}H_2\,(\rightarrow \text{trimer}) + Hg$$

Since examples of symmetrization of organomercury salts by treatment with copper [8, 9] or zinc dust [9] are described in the literature, we attempted to symmetrize γ-mercurated alcohols (I) and to decompose thermally the symmetrization products in one step by heating the γ-mercurated alcohols with zinc dust. Thus on determining the structure of γ-mercurated alcohols by the method of thermal decomposition it might be possible to dispense with the preliminary step of symmetrization. Actually it turned out that on heating 3-hydroxy-3-phenylpropylmercuric acetate (Ia), prepared from phenylcyclopropane [6], with zinc dust, there were formed ethylphenylcarbinol and ethyl phenyl ketone, i.e., the same reaction products whose formation we observed [7] in the thermal decomposition of di-(3-hydroxy-3-phenylpropyl)mercury (IIa).

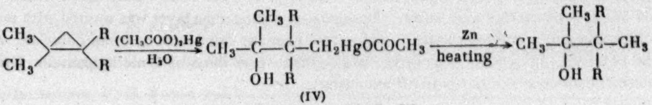


Confirmation of the given reaction mechanism (through the symmetrization step) was provided by the formation of ethylphenyl carbinol and ethyl phenyl ketone from the symmetrization product – di-(3-hydroxy-3-phenylpropyl)mercury (IIa) – on mild heating with zinc dust.

The reaction of thermal decomposition in the presence of zinc dust was studied further in the case of 3-hydroxy-2,3-dimethylbutylmercuric acetate (III), prepared from 1,1,2-trimethylcyclopropane. It was established that dimethylisopropylcarbinol (an alcohol having the carbon skeleton of the original organomercury compound), acetone, and propylene (and also a dimer of the latter) are formed from this γ-mercurated tertiary alcohol, i.e., that the decomposition is of the same type as that of the fully substituted organomercury compound (IIb) containing tertiary alcohol groups, investigated by us earlier [7]. Consequently the reaction proceeded according to the equation



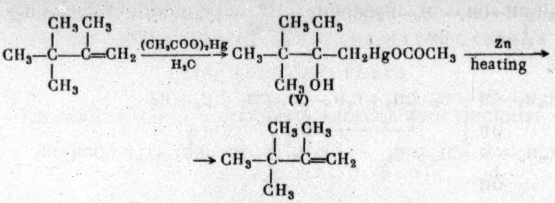
As is evident from the above, the structure of γ-mercurated alcohols containing a tertiary alcohol group is most easily established, since the tertiary alcohol formed on reaction with zinc dust may be separated from the other decomposition products by distillation. This course – the separation of the tertiary alcohol from the products of reaction of γ-mercurated tertiary alcohols with zinc dust – was tested in the case of the 3-hydroxyalkylmercuric acetates prepared from 1,1-dimethylcyclopropane [5] and 1,1,2,2-tetramethylcyclopropane [1, 2]; in the first case, dimethylethylcarbinol was isolated; in the second, dimethyl-tert-butylcarbinol (triptanol).



(IV)

(IVa) R=H; (IVb) $R=CH_3$

Thus the thermal decomposition of γ-mercurated alcohols in the presence of zinc dust may serve as a simple (one step) and convenient method of determining their structure. A further attempt was made to apply the reaction with zinc dust to the β-mercurated alcohol (V) prepared by treating triptene, an olefin isomeric with tetramethylcyclopropane, with mercuric acetate. It was found that on distillation with zinc dust, β-mercurated alcohol (V) was converted to the original olefin; i.e., its behavior in this reaction was different from that of the isomeric γ-mercurated alcohol (IVb).



EXPERIMENTAL

Action of zinc dust on a γ-mercurated secondary alcohol on heating. Into a Wurtz flask with attached air condenser were put 39.5 g of 3-hydroxy-3-phenylpropylmercuric acetate (Ia) and 14 g of zinc dust. On mild heating there began a vigorous reaction in which the decomposition products were distilled off. After the distillation was completed, the distillate was separated from the small amount of mercury and redistilled. There was isolated a fraction with b.p. 212-220° (754 mm), n_D^{20} 1.5270, consisting of ethylphenylcarbinol (b.p. 210-212° at 758 mm, n_D^{20} 1.5257 [10]) and ethyl phenyl ketone (b.p. 215° at 750 mm, n_D^{20} 1.5270 [11]); yield 12 g (~90%). The presence of ethylphenylcarbinol and ethyl phenyl ketone in this fraction was ascertained by preparing the crystalline derivatives: α-phenylpropyl 3,5-dinitrobenzoate, m.p. 66-67° (from alcohol) and ethyl phenyl ketone 2,4-dinitrophenylhydrazone, m.p. 191-192° (from alcohol). According to literature data [7], these derivatives melt at 67 and 192°, respectively. A further product of symmetrization of 3-hydroxy-3-phenylpropylmercuric acetate – di-(3-hydroxy-3-phenylpropyl)mercury (IIa), 27 g [6] – was brought into reaction with zinc dust (8 g); on mild heating a vigorous reaction took place and decomposition products, (b.p. 214-221° at 754 mm, n_D^{20} 1.5260; yield 14 g, ~90%), whose composition included ethylphenylcarbinol (characterized by the 3,5-dinitrobenzoate, m.p. 66-67°) and ethyl phenyl ketone (characterized by the 2,4-dinitrophenylhydrazone, m.p. 191-192°), were distilled off.

Action of zinc dust on γ-mercurated tertiary alcohols on heating. 3-Hydroxy-2,3-dimethylbutylmercuric acetate (III). In a distilling apparatus, connected with a gas holder for the collection of evolved gas, were placed 118 g of 3-hydroxy-2,3-dimethylbutylmercuric acetate (prepared from 1,1,2-trimethylcyclopropane [3]) and 40 g of zinc dust. The mixture was cautiously heated until the reaction began, after which the heating was stopped; a violent reaction took place, in which gas was evolved and liquid decomposition products were distilled off. To complete the reaction, the reaction mixture was again heated; the collected distillate (23 g) was redistilled in the interval 50-120°. Repetition of the experiment with the same amounts of starting materials gave the same results. The evolved gas was passed into a vessel containing bromine; the dibromide obtained amounted to 8 g (12%); after the usual treatment and distillation it had the constants of 1,2-dibromopropane.

B.p. 140-141° (754 mm), n_D^{20} 1.5190. Literature data [12]; b.p. 139-140° (749 mm); n_D^{20} 1.5172.

On redistillation of the liquid distillate (46 g) three fractions were obtained: the first, b.p. 50-65°, 17 g; the second, b.p. 65-115°, 4 g; the third, b.p. 115-120°, 24 g. The acetone* contained in the first fraction was identified by preparing the 2,4-dinitrophenylhydrazone with m.p. 125-126°. The acetone was washed out of the first and second fractions by shaking with water; the separated hydrocarbon layer was washed with saturated potassium bisulfite solution, a solution of alkali, and water again and dried with calcium chloride. After distillation over sodium the isolated hydrocarbon – 6 g (44%) – had constants near those of 4-methylpentene-1 (one of the possible polymerization products of the split-off propylene).

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* The appearance of acetone in the reaction product could be due not only to the decomposition of a γ-mercurated tertiary alcohol, but also to that of the zinc acetate formed.

B.p. 52-53° (740 mm), n_D^{20} 1.3838, d_4^{20} 0.6651. Dibromide: b.p. 86-89° (20 mm), n_D^{20} 1.4975, d_4^{20} 1.5680. Literature data for 4-methylpentene-1 [13]: b.p. 53.6-53.9°, n_D^{20} 1.3825, d_4^{20} 0.6646. Dibromide: b.p. 87° (21 mm), n_D^{20} 1.4980, d_4^{20} 1.5689.

The third fraction consisted of dimethylisopropylcarbinol (70% yield), b.p. 117-118° (745 mm); m.p. of the 3,5-dinitrobenzoate, 110-111° (a mixed sample with the 3,5-dinitrobenzoate of known dimethylisopropylcarbinol melted without depression).

Literature data [3]: b.p. 118-119° (760 mm); melting point of 3,5-dinitrobenzoate 110-111°.

3-Hydroxy-3-methylbutylmercuric acetate (IVa). On distillation of the product of the reaction between zinc dust and 3-hydroxy-3-methylbutylmercuric acetate (prepared from 1,1-dimethylcyclopropane [5]) there was isolated a fraction with b.p. 100-102°, which consisted of dimethylethylcarbinol; its 3,5-dinitrobenzoate melted at 117°.

Literature data [5]: b.p. 102-103° (756 mm); m.p. of dinitrobenzoate, 118°.

3-Hydroxy-2,2,3-trimethylbutylmercuric acetate (IVb). From the distillate obtained on heating this γ-mercurated alcohol (m.p. 69-70°; prepared from 1,1,2,2-tetramethylcyclopropane [1, 2]) with zinc dust, the crystal hydrate of dimethyl-tert-butylcarbinol (triptanol), m.p. 80° (after sublimation) was obtained on addition of water. Literature data: m.p. 81° [14].

Treatment of β-mercurated tertiary alcohol (V) with zinc dust. The reaction of 2-hydroxy-2,3,3-trimethylbutylmercuric acetate (7.5 g; prepared from triptene [2]) with zinc dust was carried out by the same method as for γ-mercurated alcohols. The reaction product was 2,3,3-trimethylbutene-1, (triptene), b.p. 77-78° at 750 mm, n_D^{20} 1.4015; yield 1.4 g (70%). Literature data [2]: b.p. 77.2-77.6° (748.5 mm), n_D^{15} 1.4030. The triptene obtained was characterized by the mercury derivative (obtained by treatment with mercuric acetate) with m.p. 101-102°.

SUMMARY

1. Treatment of γ-mercurated alcohols (3-hydroxyalkylmercuric acetates, prepared from cyclopropane hydrocarbons by reaction with mercuric acetate in aqueous solution) with zinc dust, with heating, may serve as a convenient method of determining their structure.

2. γ-Mercurated alcohols containing a secondary alcohol group give a secondary alcohol and a ketone, each having the carbon skeleton of the original organomercury compound.

3. γ-Mercurated alcohols containing a tertiary alcohol group form tertiary alcohols with the carbon skeleton of the original mercurated alcohol, while ketones are formed as a result of the cleavage of a carbon-carbon bond.

4. On heating a β-mercurated alcohol (prepared from triptene by treatment with mercuric acetate) with zinc dust the mercury salt is split off and the original olefin (triptene) is formed.

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SYNTHESIS OF POLYFUNCTIONAL SULFUR COMPOUNDS FROM DIVINYL ETHER AND HYDROGEN SULFIDE

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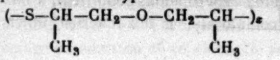
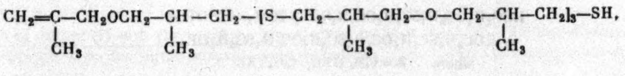
The conditions of anomalous addition of hydrogen sulfide to vinyl ethers were studied earlier in our laboratory [1-3]. It was shown that the most efficient radical catalyst is azoisobutyronitrile (the dinitrile of azoisobutyric acid).

In the present work the addition of hydrogen sulfide to divinyl ether in the presence of this catalyst was studied. Certain other reactions of addition to divinyl ether also are described: halogenation and hydrohalogenation [4] and addition to CCl_4 [5]. As regards the addition of hydrogen sulfide to di-unsaturated ethers, data exist only for diallyl ether and certain of its homologs. Thus, at temperatures from 100 to 110° in the presence of butylamine, addition of hydrogen sulfide to diallyl and methyldiallyl ethers and to diallylamine gave cyclic products of the type of thioxanes and thiazanes, respectively, together with a linear polymer having the structure  $(-S-\underset{CH_3}{\underset{|}{CH}}-CH_2-O-CH_2-\underset{CH_3}{\underset{|}{CH}}-)_x$ [6]. At a low temperature and elevated pressure, with illumination by ultraviolet light, the reaction of diallyl and methyldiallyl ethers with hydrogen sulfide, according to patent data [7, 8], led to the formation of viscous products of the type

$$CH_2{=}CH-CH_2-O-(CH_2)_3-[S-(CH_2)_3-O-(CH_2)_3]_3SH$$

and



$$CH_2{=}\underset{CH_3}{\underset{|}{C}}-CH_2OCH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-[S-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-O-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2]_3-SH,$$

which found some practical application.

The reaction of hydrogen sulfide with divinyl ether was carried out by us in the presence of azoisobutyronitrile (the dinitrile of azoisobutyric acid) at room temperature. The reaction took place in stages with the formation of a mixture of linear dithiols of varying composition.

$$(1)\ CH_2{=}CH-O-CH{=}CH_2 + 2H_2S \rightarrow \underset{(I)}{HSC_2H_4OC_2H_4SH}$$

$$(2)\ \begin{matrix} a) \\ b \\ \\ c \end{matrix}\ \begin{array}{l} (I) + CH_2{=}CH-O-CH{=}CH_2 \rightarrow HSC_2H_4OC_2H_4SC_2H_4OCH{=}CH_2 \\ \left.\begin{matrix} \\ \\ \end{matrix}\right\} HSC_2H_4OC_2H_4SC_2H_4OCH{=}CH_2 + \begin{array}{l} \xrightarrow{H_2S} \underset{(II)}{HSC_2H_4OC_2H_4SC_2H_4OC_2H_4SH} \\ \xrightarrow[(I)]{} \underset{(III)}{HSC_2H_4OC_2H_4SC_2H_4OC_2H_4SC_2H_4OC_2H_4SH} \end{array} \end{array}$$

The formation of (III) may be represented in the following manner:

$$(3)\ \begin{array}{l} a)\ (II) + CH_2{=}CH-O-CH{=}CH_2 \rightarrow HSC_2H_4OC_2H_4SC_2H_4OC_2H_4SC_2H_4OCH{=}CH_2 \\ b)\ HSC_2H_4OC_2H_4SC_2H_4OC_2H_4SC_2H_4OCH{=}CH_2 + H_2S \rightarrow (III) \end{array}$$

TABLE 1

Addition of Hydrogen Sulfide to Divinyl Ether in the Presence of 0.4 wt % of Azoisobutyronitrile(the Dinitrile of Azoisobutyric Acid)at 18-20°

Ratio of divinyl ether and H_2S (in moles)	Reaction time (in days)	Yield of reaction products (in %)			
		I	II	III	total
1 : 4.2	29	31.4	27.6	22.5	81.5
1 : 8.5	14	47.4	26.7	16.6	90.6
1 : 5.1	42	41.0	26.1	18.5	85.6
1 : 4.3	20	33.5	28.9	28.4	90.8

Compounds (I-III), were obtained in the presence of a considerable excess of hydrogen sulfide; in this case the yields were directly proportional to the ratio of the starting materials, as follows from the data of Table 1.

Using an 8-fold excess of hydrogen sulfide, one can bring the yield of 2,2'-dimercaptodiethyl ether (I) up to 40-45%. Under the reaction conditions used by us, we did not observe the formation of cyclic or polymeric products: on varying the ratios of the starting materials, we were able to synthesize complex sulfide-dithiols (II, III) in considerable amounts. It is generally known [9] that such substances are by-products of the synthesis of dithiols by the reaction of dihalogen derivatives with hydrosulfides; however, the sulfide-thiols were not investigated by the cited authors. The dithiols synthesized by us were characterized in detail. In the case of the reaction of vinyl ethers with dithiols the latter displayed an even greater tendency toward similar addition to the double bond. In contrast to thiols, which in this reaction gave, depending on the experimental conditions, a mixture of anomalous and normal addition products [10], dithiols react strictly anomalously. In this reaction, which is exothermic, dithioethers are synthesized

$$HSC_2H_4OC_2H_4SH + 2CH_2{=}CHOR \rightarrow ROC_2H_4SC_2H_4OC_2H_4SC_2H_4OR,$$

$$\text{where : } R = C_2H_5\ (IV),\quad C_4H_9\ (VI),\quad C_6H_5\ (VIII),$$

and from sulfide-dithiol (II), correspondingly, trithioethers are formed

$$HSC_2H_4OC_2H_4SC_2H_4OC_2H_4SH + 2CH_2{=}CHOR \rightarrow$$

$$\rightarrow ROC_2H_4SC_2H_4OC_2H_4SC_2H_4OC_2H_4SC_2H_4OR,$$

$$\text{where}\quad R = C_2H_5\ (IX),\quad C_4H_9\ (X).$$

Complex compounds with mercuric chloride – crystalline substances – are obtained from di- and trithioethers. The degree of purity of the dithiol and sulfide-dithiols obtained was determined iodometrically by the usual method [11], slightly modified by us in that benzene was used as the solvent.

EXPERIMENTAL

The reaction between liquid hydrogen sulfide and divinyl ether was carried out in sealed ampules at 18-20° by a method described in detail earlier by us [1]. Divinyl ether: b.p. 28-28.5°, n_D^{20} 1.3982. As an example we shall describe Experiment 15. Fifteen g of the ether, 0.06 g of the dinitrile, and 64.5 g of liquid hydrogen sulfide were taken. The ampule was opened after 14 days. After removal of the excess hydrogen sulfide the increase in weight of the reaction mass amounted to 12 g. On fractional distillation the following fractions were obtained: the first, 64-65° (2 mm), 14.6 g; the second, 168-170° (2.5 mm), 7.2 g. The residue – a colorless, viscous fraction – amounted to 4.3 g. The first fraction was completely redistilled at 64-65° (2 mm) and consisted of 2,2'-dimercaptodiethyl ether (I).

B.p. 64-65° (2 mm), 71-72° (4 mm), n_D^{20} 1.5214, d_4^{20} 1.1138, MR_D 37.82; calculated 37.69. Literature data: b.p. 103-104° at 18 mm, n_D^{20} 1.5339, d_4^{20} 1.1854, d_4^{25} 1.1648 [9]; b.p. 217° [12], b.p. 53-54° (0.05 mm), d_{20}^{20} 1.127 [11]; b.p. 95-95.3° (12.7 mm) [13].

Found %: C 34.80, 34.76; H 7.26, 7.28; S 45.95, 46.17. $C_4H_{10}OS_2$. Calculated %: C 34.75; H 7.29; S 46.39.

TABLE 2

No. of experiment	Starting materials (in g)		Azoiso-butyronitrile dinitrile of azoisobutyric acid (in g)	Temperature rise to	Duration of experiment (in days)	Yield of dithioether (IV) (in %)
	dithiol (I)	vinyl ethyl ether				
1a	5.6	16	0.025	—	27	87.3
2	4	12.6	0.01	25°	3	90.6
3	2.5	3	—	40	3	88.6

(I) reacted with an alcoholic solution of mercuric chloride with splitting-off of HCl. However, the reaction was not quantitative, and the corresponding dimercurichloride was not isolated. The 2,2'-dimercaptodiethyl ether (I) was 100% pure (according to iodometric titration).

The second fraction distilled at 165-167° (2 mm) and consisted of the corresponding sulfide-dithiol (II):

B.p. 165-167° (2.5 mm), 170-174° (3-3.5 mm), 164-166° (2 mm), n_D^{20} 1.5380, d_4^{20} 1.1574, MR_D 65.51; 65.78. Literature data: b.p. 182-185° (8 mm) [9].

Found %: C 39.53, 39.40; H 7.47, 7.35; S 39.38, 39.43. $C_8H_{18}O_2S_3$. Calculated %: C 33.62; H 7.49; S 39.68.

Sulfide-dithiol (II), a clear, colorless liquid, soluble in all organic solvents, had a less sharp odor and gave instantaneously a qualitative reaction with mercuric chloride in the presence of methyl orange. The sulfide-dithiol (II) was 99.5-99.8% pure (by iodometric titration).

The third fraction, a colorless, oily, rather viscous liquid, did not distill; it was practically insoluble in alcohol, ether, and acetone and readily soluble in benzene. It gave an acid reaction in the presence of methyl orange on addition of an alcoholic solution of mercuric chloride, which indicated that a molecule of this substance contains free thiol groups. The fraction was analyzed without additional purification and apparently consisted of somewhat impure sulfide-dithiol (III). Actually, iodometric determination of this preparation gave 94-95% purity.

Found %: C 42.60, 42.73; H 7.54, 7.53; S 36.15, 35.92. $C_{12}H_{26}O_3S_4$. Calculated %: C 41.59; H 7.56; S 37.01.

Reaction of dithiol (I) with vinyl ethers. The reaction between vinyl alkyl ethers and dithiol (I) took place even without catalyst when the initial reagents were mixed, but it proceeded with exceptional vigor in the presence of the catalyst (dinitrile).

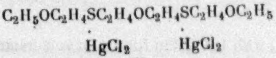
a) (I) + vinyl ethyl ether → (IV). The conditions and results of certain experiments are given in Table 2.

After the excess vinyl ethyl ether was driven off, the reaction product consisted of a single substance – bis-[2-(ethoxyethyl)-(2-thioethyl)] ether (IV).[*]

B.p. 176-177° (3 mm), 171-173° (2-2.3 mm), 164° (1.5 mm), n_D^{20} 1.4899, d_4^{20} 1.0399, MR_D 78.52; 78.48.

Found %: C 50.99, 51.27; H 9.27, 9.25; S 22.48, 22.35. $C_{12}H_{26}O_3S_2$. Calculated %: C 51.02; H 9.28; S 22.7.

Dithioether (IV) is a colorless, oily liquid without any sharp odor, soluble in all organic solvents. (IV) reacted vigorously with an alcoholic solution of $HgCl_2$, giving a neutral reaction in the filtrate in the presence of methyl orange and a quantitative yield of complex compound (V) in the precipitate.



$$C_2H_5OC_2H_4\underset{\substack{\cdot\\ HgCl_2}}{S}C_2H_4OC_2H_4\underset{\substack{\cdot\\ HgCl_2}}{S}C_2H_4OC_2H_5$$

(V)

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[*] A. E. Kretov [14] isolated a fraction with b.p. 200-220°, corresponding to the composition of the dithioether, from the by-products.

It crystallized from a concentrated solution in hot alcohol in the form of acicular crystals with m.p. 80.5-80.7°.

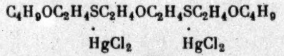
Found %: C 17.10, 17.17; H 3.09, 3.06; Cl 17.39, 17.14. $C_{12}H_{26}O_2S_2Hg_2Cl_4$. Calculated %: C 17.46; H 3.18; Cl 17.18.

b) (I) + vinyl butyl ether → (VI). When 6 g of dithiol (I), 0.03 g of the dinitrile, and 20 g of vinyl butyl ether were mixed, the temperature rose to 65°. From the reaction product, 12.5 g (85%) of bis-[2-(butoxyethyl)-(2-thioethyl)] ether (VI) was isolated at 207-208° (3 mm).

B.p. 207-208° (3 mm), 186-188° (1.3-1.5 mm), n_D^{20} 1.4820, d_4^{20} 0.9714, MR_D 97.0; calc. 96.9.

Found %: C 56.56, 56.53; H 10.04, 10.00; S 19.13, 18.90. $C_{16}H_{34}O_3S_2$. Calculated %: C 56.76; H 10.12; S 18.94.

In the reaction with $HgCl_2$, (VI) behaved like (IV). Complex compound (VII), m.p. 71°, was isolated.



$$\mathrm{C_4H_9OC_2H_4\underset{HgCl_2}{\underset{\cdot}{S}}C_2H_4OC_2H_4\underset{HgCl_2}{\underset{\cdot}{S}}C_2H_4OC_4H_9}$$

(VII)

Found %: C 22.05, 22.08; H 3.78, 3.71; Cl 16.28, 15.92. $C_{16}H_{34}O_3S_2Hg_2Cl_4$. Calculated %: C 21.80; H 3.89; Cl 16.09.

c) (I) + vinyl phenyl ether → (VIII). On mixing 4.5 g of (I) with 8 g of vinyl phenyl ether in the presence of 0.01 g of the dinitrile, the temperature of the reaction mass rose to 43°. The product remained clear and viscous for a long time and then crystallized. After several washings with alcohol the product was isolated quantitatively: m.p. 61.5° after crystallization from boiling ethanol.

Found %: C 63.59, 63.60; H 6.83, 6.89; S 16.90, 16.93. $C_{20}H_{26}O_3S_2$. Calculated %: C 63.46; H 6.92; S 16.94.

d) (I) + divinyl ether. The behavior of divinyl ether proved to be peculiar. At room temperature it was impossible to obtain an individual addition product as in the case of other vinyl ethers. A viscous product of polymeric character was obtained, which dissolved readily in benzene and was precipitated by ether, m.p. 46°; on analysis it was found to contain 36% sulfur, but it was not investigated in detail.

Reaction of sulfide-dithiol (II) with vinyl ethers. On mixing the initial reagents the temperature rose to 40° within 25-35 minutes.

a) (II) + vinyl ethyl ether → (IX). From 3.6 g of (II) and 3 g of vinyl ethyl ether in the presence of 0.01 g of the dinitrile there was isolated the fraction: 215-230° (2-2.5 mm), n_D^{20} 1.5056 in the amount of 5 g, or 87.7% of the desired trithioether (IX). After repeated fractional distillation it had the following constants:

B.p. 231-234° (2 mm), n_D^{20} 1.5060, d_4^{20} 1.0781, MR_D 106.5; calc. 106.5.

Found %: C 49.88, 49.77; H 8.82, 8.94; S 25.10, 24.96. $C_{16}H_{34}O_4S_3$. Calculated %: C 49.70; H 8.86; S 24.88.

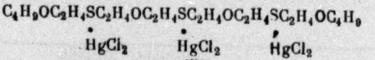
On interaction with mercuric chloride in the presence of methyl orange, (IX) gave a neutral reaction; however, the precipitated complex compound could not be obtained in pure form.

b) (II) + vinyl butyl ether → (X). From 2.5 g of (II) and 3 g of vinyl butyl ether in the presence of 0.01 g of the dinitrile, 4.1 g (89.9%) of the desired trithioether (X) was obtained.

B.p. 245-250° (2-2.5 mm), n_D^{20} 1.4987, d_4^{20} 1.0372, MR_D 125.25; calc. 125.04.

Found %: C 54.35, 54.24; H 9.58, 9.58; S 22.00, 21.94. $C_{20}H_{42}O_4S_3$. Calculated %: C 54.26; H 9.56; S 21.73.

On interaction of trithioether (X) with $HgCl_2$ the filtrate gave a neutral reaction in the presence of methyl orange. Complex compound (XI), m.p. 75°, was obtained in quantitative yield.



$$C_4H_9OC_2H_4\underset{\cdot HgCl_2}{S}C_2H_4OC_2H_4\underset{\cdot HgCl_2}{S}C_2H_4OC_2H_4\underset{\cdot HgCl_2}{S}C_2H_4OC_4H_9$$

(XI)

Found %: C 19.07, 19.27; H 3.29, 3.21; Cl 16.89, 16.68. $C_{20}H_{42}O_4S_3Hg_3Cl_6$. Calculated %: C 19.10; H 3.37; Cl 16.92.

SUMMARY

1. The reaction between divinyl ether and a considerable excess of liquid hydrogen sulfide has been studied; substances having a linear structure – a dithiol and sulfide-dithiols – have been synthesized.

2. Certain transformations of the dithiol and a sulfide-dithiol have been investigated; in the case of the reaction with vinyl ethers it has been shown that they have an even greater tendency toward anomalous addition to the double bond than thiols.

3. Certain dithioethers and trithioethers have been synthesized; complex compounds of these with mercuric chloride have been obtained.

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FROM THE FIELD OF ORGANIC INSECTOFUNGICIDES

XXXVI. ON THE REACTION OF TETRACHLORO- AND PENTACHLOROCYCLOPENTADIENES WITH CERTAIN UNSATURATED COMPOUNDS*

N. N. Mel'nikov and S. D. Volodkovich

In connection with the discovery of the insecticidal properties of polychloro-derivatives of polycyclic hydrocarbons in recent years, the condensation of hexachlorocyclopentadiene with various unsaturated hydrocarbons has been studied in a great number of cases, and certain compounds of this type have found wide application in agriculture, for vegetable-pest control [1-3]. The condensation of 2,3,4,5-tetrachlorocyclopentadiene and 1,2,3,4,5-pentachlorocyclopentadiene with unsaturated compounds was studied only in the cases of cyclopentadiene, maleic anhydride, benzoquinone, and acrylonitrile [4-6].

The synthesis of the adducts of 2,3,4,5-tetrachlorocyclopentadiene and 1,2,3,4,5-pentachlorocyclopentadiene with various unsaturated compounds and the study of their insecticidal properties is of great interest both for the purpose of obtaining data concerning the dependence of insecticidal activity on structure and for that of collecting material for elucidation of the mechanism of the action of the given group of compounds on insects. It was especially interesting to compare the insecticidal activity of the fluorine-containing analogs of 'aldrin,' recently described by us, with that of compounds containing hydrogen and one halogen atom in the endomethylene bridge.

In connection with the above a special investigation of the synthesis and study of the products of condensation of 2,3,4,5-tetrachlorocyclopentadiene and 1,2,3,4,5-pentachlorocyclopentadiene with unsaturated compounds, primarily bicyclo-[2,2,1]-heptene, bicyclo-[2,2,1]-heptadiene-2,5, maleic acid esters, and certain other substances. The compounds prepared by us and their properties are given in the table.

The condensation of 1,2,3,4,5-pentachlorocyclopentadiene and 2,3,4,5-tetrachlorocyclopentadiene with unsaturated hydrocarbons and esters of unsaturated acids takes place, almost the same as in the case of hexachlorocyclopentadiene, on heating a mixture of the reacting substances to 110-130° for several hours.

The study of the insecticidal effects of various substances on house flies, carried out by E. F. Granin under the direction of K. A. Gar, showed that the most active insecticide is 1,2,3,4,10-pentachloro-1,4,5,8-diendomethylenehexahydronaphthalene [1], which has nearly twice the insecticidal activity of chloroindane, but is inferior to 'aldrin.' 1,2,3,4-Tetrachloro-1,4,5,8-diendomethylenehexahydronaphthalene is practically inactive. These observations give a direct indication of the great effect on the toxicity of 'aldrin'-type compounds of substituents in the endomethylene bridge, which was noted by us also in the study of the corresponding fluoro-derivatives [7].

EXPERIMENTAL

Preparation of starting materials. 2,3,4,5-Tetrachlorocyclopentadiene was prepared by us by reduction of hexachlorocyclopentadiene with zinc dust in acetic acid [4, 8]. After recrystallization from methyl alcohol the 2,3,4,5-tetrachlorocyclopentadiene had m.p. 61-62°.

1,2,3,4,5-Pentachlorocyclopentadiene was obtained by the fractionation of technical hexachlorocyclopentadiene prepared by the chlorination of cyclopentadiene with sodium hypochlorite, and also by the reduction of C_5Cl_6 with $SnCl_2$ in acetone. 1,2,3,4,5-Pentachlorocyclopentadiene had the following constants.

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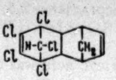
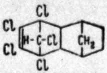
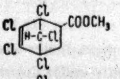
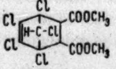
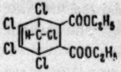
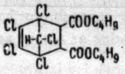
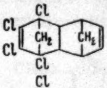
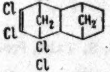
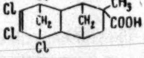
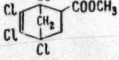
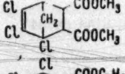
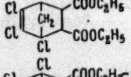
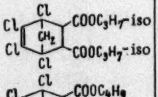
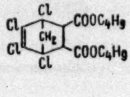
*From the master's thesis of S. D. Volodkovich.

No. of compound	Formula		Boiling point (pressure in mm)	Melting point	n_D^{20}	d_4^{20}	MR found	MR calculated	Yield (in %)	Chlorine content (in %) found	Chlorine content (in %) calculated
1		a)	172–173° (10)	—	1.5752	1.4970	72.85	72.21	70	53.47	53.70
		b)		82—83	—	—	—	—	15	63.51	
2			—	93—94	—	—	—	—	60	53.84 54.22	53.38
3			135—136 (4)	—	1.5375	1.5912	63.87	64.76	70	54.92 54.22	54.69
4			184—185 (4)	88—89					39	46.03 45.65	46.40
5			168—169 (4)	—	1.5410	1.5292	84.23	84.77	34	43.81 43.45	43.11
6			175—176 (4)	122—123					34	37.38 36.88	37.94
7			142—143 (4)	—	1.5620	1.4278	67.68	67.35	43	48.44 48.58	47.97
8			140—141 (4)	—	1.5630	1.4170	68.35	67.81	47	47.37 47.63	47.65
9			208—210 (24)	—	1.5442	1.4180	79.25	78.73	54	39.87 40.48	39.88
10			146—147 (20)	—	1.5300	1.4947	59.82	59.90	50	49.43 49.25	48.96
11			—	105—106	—	—	—	—	43	40.91 41.29	40.80
12			163—194	—	1.5349	1.4534	80.45	79.90	37	37.05 36.80	37.76
13			174—176	—	1.5210	1.3644	89.85	89.13	31	35.00 34.31	35.15
14			188—190	—	1.5060	1.3141	97.67	98.36	32	32.29 33.00	32.87

B.p. 104-106° (23 mm), d_4^{20} 1.6642, n_D^{20} 1.5615, MR_D 46.62; calc. 46. 48.

Condensation of polyhalocyclopentadienes with unsaturated compounds. The condensation of 1,2,3,4,5-pentachlorocyclopentadiene and 2,3,4,5-tetrachlorocyclopentadiene with unsaturated compounds was carried out by heating equimolar quantities of the reagents in a flask provided with a reflux condenser and a mechanical stirrer. Reaction temperature, 120-130°. Duration, 3-4 hours.

In the condensation of polychlorocyclopentadienes with bicyclo-[2,2,1]-heptadiene-2,5, a 2.5-fold excess of the latter was used.

The condensation of 2,3,4,5-tetrachlorocyclopentadiene with esters of maleic acid was carried out in toluene by boiling the solution for 6-8 hours.

The compounds prepared by us and their properties are given in the table.

SUMMARY

1. The reactions of 2,3,4,5-tetrachloro- and 1,2,3,4,5-pentachlorocyclopentadienes with certain unsaturated compounds have been studied. It has been shown that these reactions go smoothly under the same conditions as the reactions of unsaturated compounds with hexachlorocyclopentadiene. A number of tetra- and pentachloroderivatives of polycyclic compounds, not described in the literature, have been synthesized.

2. The study of the insecticidal activity of the synthesized compounds showed that the toxicity of 'aldrin'-type compounds is greatly affected by substituents in the endomethylene bridge. The insecticidal activity decreases in the order: dichloro-, monochloro-, difluoro-derivatives.

Of the synthesized compounds not described in the literature, 1,2,3,4,10-pentachloro-1,4,5,8-diendomethylenehexahydronaphthalene has the highest insecticidal activity, being nearly twice as active as chloroindane, but inferior to 'aldrin.'

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SYNTHESIS OF BROMO-SUBSTITUTED β-PHENYLETHYLAMINES

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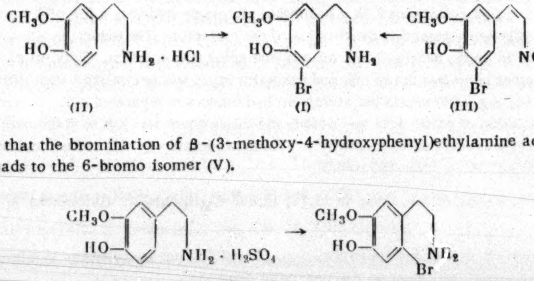
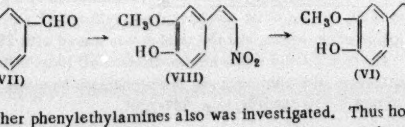
β-(3-Methoxy-4-hydroxy-5-bromophenyl)ethylamine (I) is an important intermediate in the synthesis of the dimethyl ether of the racemic alkaloid, tubocurarine iodide [1]. The preparation of substances of analogous structure is a laborious, multistage process resulting in low yield [2-4]. Although the direct halogenation of compounds containing a vanillyl radical is described in the literature, the question of orientation on bromination in such molecules remains insufficiently clear. In connection with this it is definitely of interest to work out the conditions of bromination of substituted β-phenylethylamines in order to prepare the required bromo-derivatives.

A number of authors have shown that eugenol [5], isoeugenol [6-7], and olivil [8] give 5-bromo derivatives while creosol [9, 10] and homovanillic acid [11], as well as the corresponding dimethoxy, dibenzyloxy, and other derivatives, give 6-bromo isomers [12-18]. Thus the most probable position on bromination is C_5 or C_6. Actually, when the reaction is carried out without solvent, a mixture of these isomers and an insignificant amount of the dibromo derivative are formed. Practically pure β-(3-methoxy-4-hydroxy-5-bromophenyl)ethylamine (I) is obtained by the bromination of β-(3-methoxy-4-hydroxyphenyl)ethylamine hydrochloride (II) in acetic acid solution. An identical substance (according to melting point and ultraviolet spectrum) was obtained also by the reduction of 3-methoxy-4-hydroxy-5-bromo-ω-nitrostyrene (III) with lithium aluminum hydride.



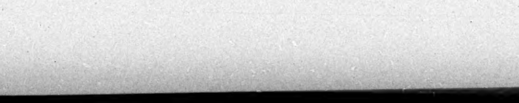
(II) (I) (III)

We found also that the bromination of β-(3-methoxy-4-hydroxyphenyl)ethylamine acid sulfate (IV) under similar conditions leads to the 6-bromo isomer (V).



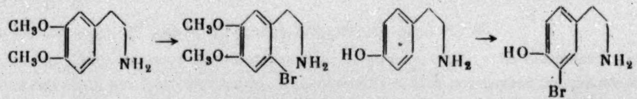
(IV) (V)

The required β-3(methoxy-4-hydroxyphenyl)ethylamine (VI) was synthesized from vanillin (VII) through the corresponding nitrostyrene (VIII).



(VII) (VIII) (VI)

The bromination of other phenylethylamines also was investigated. Thus homoveratrylamine (IX) gives β-(3,4-dimethoxy-6-bromophenyl)ethylamine (X), and tyramine (XI) gives 3-bromotyramine (XII) in good yield.



(IX) (X) (XI) (XII)

EXPERIMENTAL

β-(3-Methoxy-4-hydroxyphenyl)ethylamine (VI) was prepared through hydrogenation of 3-methoxy-4-hydroxy-ω-nitrostyrene by the Hahn method [19], modified only in the use of a suspension of the nitrostyrene in acetic acid, which permits a considerable increase in the charge. Yield of β-(3-methoxy-4-hydroxyphenyl)ethylamine acid sulfate, 92%. M.p. 150-151° (from a mixture of methyl alcohol and ethyl acetate, 1:1).

Yield of base, 97%. M.p. 159-160° [19-20]. Hydrochloride, m.p. 213-214° [21].

β-(3-Methoxy-4-hydroxy-5-bromophenyl)ethylamine (I). A) To a solution of 6.24 g of β-(3-methoxy-4-hydroxyphenyl)ethylamine hydrochloride in 40 ml of glacial acetic acid, heated to 70°, was added 7.55 g of dioxan dibromide [22] with stirring, after which the solvent was distilled off in vacuo. The residue was treated with 20 ml of ethyl acetate and left to stand at 0° for 72 hours. The precipitated hydrochloride was filtered off, dissolved in 10 ml of water, and neutralized with aqueous ammonia. The base was separated out and washed with water (30 ml). A colorless, crystalline substance soluble in xylene and bromobenzene on heating. M.p. 169.5-170° (from m-xylene).

Found %: C 43.55, 44.15; H 5.21, 5.12; N 5.97, 5.73; Br 32.12, 31.70. $C_9H_{12}O_2NBr$. Calculated %: C 43.9; H 4.88; N 5.70; Br 32.55.

The hydrochloride is a colorless, crystalline substance, m.p. 215.5-217° (from a mixture of methyl alcohol and ethyl acetate, 1:1). λ_{max} (water) 285 mμ, log ε 3.414.

The picrate is a yellow, crystalline substance, m.p. 194-196° (from methyl alcohol).

B) A three-neck flask provided with a stirrer, reflux condenser, and Soxhlet extractor was charged with 280 ml of an ethereal solution containing 0.45 g of lithium aluminum hydride, 1.5 g of 3-methoxy-4-hydroxy-5-bromo-ω-nitrostyrene [23] being placed in the thimble of the extractor. The reduction was carried out by boiling the ethereal solution for 18 hours, nearly all the nitrostyrene going into solution. Fifty ml of 2 N sulfuric acid was then added. The ether layer was drawn off, and the water layer was neutralized with lithium carbonate to a pH of 6 and heated to boiling, after which the aluminum hydroxide was separated out. To the filtrate 15 ml of a saturated alcoholic solution of picric acid was added, and the mixture was left to stand overnight. The precipitated β-(3-methoxy-4-hydroxy-5-bromophenyl)ethylamine picrate was filtered off and recrystallized twice from water. Yield 1.35 g (51.9%), m.p. 195-196.5°.

Found %: C 38.05, 37.62; H 3.2, 2.95; N 11.76, 11.80. $C_{15}H_{15}O_9N_4Br$. Calculated %: C 37.95; H 3.16; N 11.78.

The base is a colorless, crystalline substance, m.p. 169-170° (from m-xylene). A mixture test with the base from the preceding experiment gave no melting-point depression.

Found %: C 43.90, 44.00; H 4.77, 4.55; N 5.41, 5.37; Br 32.3, 32.33. $C_9H_{12}O_2NBr$. Calculated %: C 43.90; H 4.89; N 5.70; Br 32.55.

β-(3-Methoxy-4-hydroxy-6-bromophenyl)ethylamine (V). To a solution of 2 g of β-(3-methoxy-4-hydroxyphenyl)ethylamine acid sulfate in 20 ml of glacial acetic acid was added 1.87 g of dioxan dibromide during 2-3 minutes, the solvent was distilled off in vacuo, and the residue was mixed with 20 ml of ethyl acetate and left to stand at 20° for 72 hours. The precipitated substance was filtered off (m.p. 192-196°) and dissolved in 10 ml of water, and, after neutralization with ammonia, the 6-bromoamine base was isolated in the form of a colorless, crystalline substance. Yield 1.17 g (58.8%), m.p. 187-189°.

Found %: C 43.95, 44.04; H 4.52, 4.88; N 5.44, 5.75. $C_9H_{12}O_2NBr$. Calculated %: C 43.90; H 4.88; N 5.70.

The hydrochloride is a colorless, crystalline substance, m.p. 232-233° (dec., from a mixture of methyl alcohol and ethyl acetate, 1:1). λ_{max} (water) 285 mμ, log ε 3.714.

Found %: C 38.14; H 4.40; N 4.63. $C_9H_{12}O_2NBr \cdot HCl$. Calculated %: C 38.25; H 4.60; N 4.96.

The picrate is a yellow, crystalline substance, m.p. 205-207° (from aqueous methyl alcohol, 1:1).

β-(3,4-Dimethoxy-6-bromophenyl)ethylamine (X) was prepared from homoveratrylamine hydrochloride and dioxan dibromide by mixing them in equimolar quantities without solvent. Colorless needles, m.p. 137-137.5°.

Found %: C 46.32, 45.9; H 5.50, 5.50; N 5.20. $C_{10}H_{14}O_2NBr$. Calculated %: C 46.2; H 5.39; N 5.39.

The hydrochloride is a colorless, crystalline substance, m.p. 193-194° (from a mixture of methyl alcohol and ethyl acetate, 1:1).

Found %: C 40.20; H 4.80; N 5.05. $C_{10}H_{14}O_2NBr \cdot HCl$. Calculated %: C 40.50; H 5.06; N 4.73.

The picrate is a yellow, crystalline substance, m.p. 196-196.5°.

Found %: C 39.39, 39.28; H 3.80, 3.52; N 11.12, 11.52. $C_{10}H_{14}O_2NBr \cdot C_6H_3O_7N_3$. Calculated %: C 39.30; H 3.48; N 11.45.

3-Bromotyramine (XII) was prepared by mixing equimolar quantities of tyramine hydrochloride and dioxan dibromide without solvent. A colorless, crystalline substance, m.p. 162-164° (from m-xylene).

Found %: N 6.13. $C_8H_{10}ONBr$. Calculated %: N 6.49.

The hydrochloride is a colorless, crystalline substance, m.p. 205.5-207° (from a mixture of methyl alcohol and ethyl acetate, 1:1). λ_{max} (water) 280 mμ, log ε 3.3849.

Found %: N 5.69, 5.54. $C_8H_{10}ONBr \cdot HCl$. Calculated %: N 5.55.

SUMMARY

β-(3-Methoxy-4-hydroxy-5-bromophenyl)ethylamine has been synthesized by the bromination of β-(3-methoxy-4-hydroxyphenyl)ethylamine hydrochloride with dioxan dibromide in an acetic acid medium. The position of the bromine was proved by identification with the substance obtained on reduction of 3-methoxy-4-hydroxy-5-bromo-ω-nitrostyrene with lithium aluminum hydride. It was shown that the bromination of β-(3-methoxy-4-hydroxyphenyl)ethylamine acid sulfate under similar conditions leads to the 6-bromo isomer. β-(3,4-Dimethoxy-6-bromophenyl)ethylamine and 3-bromotyramine, not described earlier, were also obtained.

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STEREOCHEMICAL INVESTIGATIONS

IV. SCHIFF BASES FROM OPTICALLY ACTIVE α-BENZYLETHYLAMINE

V. M. Potapov and A. P. Terent'ev

In the preceding report [1] we described a series of Schiff bases from optically active α-phenylethylamine (I). The interesting peculiarities of optical rotation, found in this series, occasioned the synthesis and investigation of the optical activity of a second series of Schiff bases. The optically active amine used here was α-benzylethylamine (II), which differs from (I) by the presence of a CH_2 group between the benzene nucleus and the asymmetric center.

We synthesized the racemate of (II) by the reductive amination of phenylacetone (after Leikart). For the synthesis of the initial phenylacetone, methods described in the literature [2, 3] may be used. However, it takes a great deal of time to carry out these syntheses, despite their apparent simplicity. It is much more convenient to prepare the phenylacetone by the catalytic condensation of phenylacetic and acetic acids. This condensation takes place at 410-420° over manganous oxide. The yield of phenylacetone in this case reaches 70%.

(II) may be resolved into optical antipodes by treatment with D-tartaric acid in alcoholic solution, as described in a number of works [2, 4]. Menthyl hydrogen sulfate, which was used earlier in the preceding works of this series, also proved suitable for resolution. Through menthyl hydrogen sulfate (−) (II) is isolated, while on resolution with D-tartaric acid a diastereomer containing (+) (II) precipitates. Thus a combination of the two reagents makes it possible to obtain both antipodes.

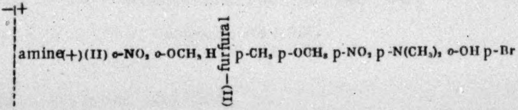
The condensation of optically active (II) with substituted benzaldehydes proceeds smoothly on heating in a water bath without solvent, in benzene, or in methanol. The Schiff base was purified by distillation of recrystallization (the latter was permissible only when the optically pure original amine was used). The constants of the substances obtained are given in the experimental part, whereas data on their optical activity (recalculated for optically pure (+)(II)) are given in Table 1.

The degree and sign of optical rotation of the given series of Schiff bases display peculiarities different from those for the series described in the preceding report. While Schiff bases obtained from (+) (I), as a rule, have the opposite sign of rotation (with the exception of ortho-nitro- and ortho-methoxy-substituted ones), all Schiff bases from (+) (II) without exception retain the (+)-rotation. In this connection, the Schiff bases from (II) appear to be similar to the corresponding α-(β-naphthyl)benzylamine derivatives investigated by Betti [5].

In the (II) series the peculiar character of the o-NO_2- and o-OCH_3-derivatives is again found, albeit in a different form from that in the (I) series; here the corresponding Schiff bases are unique, their $[M]_D$ values being less than the rotation of the Schiff base with unsubstituted benzaldehyde.

Notwithstanding the external difference, a certain similarity in the two series of Schiff bases is found on closer scrutiny. It becomes particularly apparent if the two series of derivatives are arranged in the order of increasing molecular rotation:

$$p\text{-N(CH}_3)_2\ \ o\text{-OH}\ \ p\text{-NO}_2\ \ p\text{-Br}\ \ p\text{-CH}_3\ \ \text{H}\ \ \text{(I)— furfural}\ \ \overset{-\,|\,+}{\vdots}\ \ \text{amine}(+)\ \text{(I)}\ \ o\text{-OCH}_3\ \ o\text{-NO}_2$$


– | +
amine(+)(II) o-NO₂ o-OCH₃ H
(II)–furfural
p-CH₃ p-OCH₃ p-NO₂ p-N(CH₃)₂ o-OH p-Br

The order of the compounds in the two series shows a certain similarity if one series is examined from left to right and the other from right to left; the two series are, as it were, "mirror images." This may be due to the fact that the relative configurations of (+) (I) and (+) (II) are different. The small amount of experimental data, so far accumulated, on the optical activity of Schiff bases is not sufficient to permit any far-reaching conclusions on the causes of the observed peculiarities. However, the following consideration is not devoid of interest.

TABLE 1

Molecular Rotations $[M]_D$ of Schiff Bases from (+)-α-Benzylethylamine $C_6H_5CH_2-$ $-CH(CH_3)-N=CH-C_6H_4-X$

No. of compd.	Substituent X	$[M]_D$ in solvents:				
		benzene	methanol	acetone	dichloroethane	heptane
1	o-NO_2	200	225	225	198	189
2	o-OCH_3	374	440	425	401	381
3	H	520	544	538	485	508
4	Furfural (II)	564	722	578	517	578
5	p-CH_3	567	695	592	512	842
6	p-OCH_3	683	785	673	610	662
7	p-NO_2	780	783	730	680	728
8	p-$N(CH_3)_2$	855	855	740	644	891
9	o-OH	880	1135	820	773	895
10	p-Br	1010	1090	987	908	1035

On the basis of the investigation of rotatory dispersion in a series of amines, Lowry and co-workers [6, 7] reached the conclusion that optically active amines may belong to two types. For most amines optical activity is caused primarily by circular dichroism of the absorption band at λ 2300 A, and the formation of this band is due to the free electron pair of the amino nitrogen. For amines of this first type, therefore, the degree of rotation depends strongly on salt formation, in which the electron pair is bound. In the second group of optically active amines the decisive role in the establishment of a definite degree of rotation is played by the dichroism of other absorption bands. In this case salt formation, which affects the electron pair of the amino nitrogen, does not have so much influence on the degree of rotation. Lowry refers α-(β-naphthyl)benzylamine in particular to the second group. At the same time it is known from the work of Betti that Schiff bases of this amine retain the sign of rotation of the original amine.

On the basis of the small difference between the rotations of free (II) and its hydrochloride, we may assume that (II) also should be referred to the second group. In connection with this, (II) behaves like α-(β-naphthyl)benzylamine on conversion to a Schiff base. In the case of (I) salt formation markedly changes the degree of rotation; this amine belongs to the first group, and on conversion to a Schiff base, in contrast to the preceding, the sign of rotation changes.

EXPERIMENTAL

Phenylacetone $C_6H_5CH_2COCH_3$. From the pasty mass obtained by mixing equal quantities of manganese carbonate and asbestos fiber (with addition of a small amount of waterglass and water) were prepared balls having the size of a pea, which, while still moist, were loaded into a hard-glass tube 2 cm in diameter to form a layer 40 cm long. After drying in a current of warm air the tube was placed in a tubular furnace and the temperature gradually raised to 400° in a slow current of nitrogen; 30 ml of methanol was then admitted, followed at 410-420° by a mixture of 1 part phenylacetic acid and 3 parts glacial acetic acid at a rate of 15-20 drops per minute. Water and a yellowish, oily liquid collected in the receiver. The top layer was drawn off, dried with $CaCl_2$, and distilled through a column (dephlegmator). Yield of phenylacetone, up to 70%.

α-Benzylethylamine $C_6H_5CH_2CH(NH_2)CH_3$. The synthesis was carried out by the cited method [2].

B.p. 200-201.5°, n_D^{20} 1.5186.

Literature data: b.p. 204-205°, n_D^{20} 1.5190 [8].*

(+)-α-Benzylethylamine. The resolution of the racemate with D-tartaric acid in alcohol was carried out as described [2]. The pure (+)-amine bitartrate has $[\alpha]_D^{17}$ + 28.7° (water c 8.4).** On decomposition with alkali, followed by distillation, there was isolated (+) (II) $[\alpha]_D^{19}$ + 36.3° (without solvent).

(−)-α-Benzylethylamine was prepared by resolution of the racemate by means of menthyl hydrogen sulfate, as described by us earlier [11]. The diastereomeric salts were separated by repeated recrystallization from water; in this case, in order to avoid large volumes, the more soluble salt might be extracted from the precipitate by boiling water in quantities insufficient to dissolve the precipitate completely. Isolation of the pure diastereomeric salt of the (−) amine requires many crystallizations, and the yield of salt is very small. We stopped with the fifth crystallization, which gave a salt with m.p. 190-191°, having $[\alpha]_D^{20}$ 51° (water c 4); after decomposition with alkali, (−) (II), $[\alpha]_D^{20}$ − 26° (without solvent) was obtained in 30% yield calculated on the basis of the amine used.

o-Nitrobenzal-(−)-benzylethylamine

$o\text{-}O_2N-C_6H_4-CH=N-CH(CH_3)-CH_2C_6H_5$. A mixture of 2.89 g of (−) (II), $[\alpha]_D^{20}$ − 26° (optical purity 73.3%),*** 3.23 g of o-nitrobenzaldehyde, and 20 ml of methanol was refluxed for 1.5 hours, the methanol and water were driven off, and the residue was distilled in vacuo. Yield 4.44 g (77%).

B.p. 187-189° (4 mm), d_4^{20} 1.131, n_D^{20} 1.5834, MR_D 79.3; calc. 78.4; $[\alpha]_D^{20}$ − 54.7° (benzene, c 1.4), − 61.5° (methanol, c 1.5), − 61.5° (acetone, c 1.6), − 54.2° (dichloroethane, c 1.1), − 51.7° (heptane, c 1.4).

o-Methoxybenzal-(−)-α-benzylethylamine $o\text{-}CH_3O-C_6H_4-CH=N-CH(CH_3)CH_2C_6H_5$ was prepared like the preceding from 2.86 g of (−) (II) and 2.89 g of o-methoxybenzaldehyde in 10 ml of benzene; yield 4.6 g (85.5%).

B.p. 165-166.5° (3 mm), d_4^{20} 1.047, n_D^{20} 1.5782, MR_D 80.3; calc.78.2. $[\alpha]_D^{20}$ − 108° (benzene, c 2.4), − 127° (methanol, c 2.3), − 123° (acetone, c 2.4), − 116° (dichloroethane, c 2.2), − 110° (heptane, c 1.3).

Found %: N 5.48, 5.49. $C_{17}H_{19}ON$. Calculated %: N 5.53.

Furfural-(+)-α-benzylethylamine

$C_4H_3O-CH=N-CH(CH_3)-CH_2C_6H_5$ was prepared like the preceding from 2.41 g of (+) (II) (optical purity 100%) and 1.71 g of furfural in 10 ml of benzene; yield 2.9 g (76.3%).

B.p. 133-135° (4 mm), d_4^{20} 1.038, n_D^{20} 1.5640, MR_D 66.9; calc.64.8. $[\alpha]_D^{20}$ + 265° (benzene, c 1.8), + 339° (methanol, c 1.8), + 272° (acetone, c 1.8), + 243° (dichloroethane, c 1.7), + 272° (heptane, c 1.7).

Found %: N 6.89, 6.67. $C_{14}H_{15}ON$. Calculated %: N 6.57.

Benzal-(−)-α-benzylethylamine $C_6H_5CH=N-CH(CH_3)CH_2C_6H_5$ was prepared like the preceding from 3.21 g of (−) (II) and 2.52 g of benzaldehyde; yield 3.78 g (72 %).

B.p. 142-144° (3 mm), d_4^{20} 1.002, n_D^{20} 1.5736, MR_D 73.5; calc. 71.9. $[\alpha]_D^{19}$ − 170° (benzene, c 2.2), − 177.5° (methanol, c 4.0), − 176° (acetone, c 3.1), − 158.5° (dichloroethane, c 2.2), − 166° (heptane, c 1.4).

Found %: C 86.41, 86.38; H 8.01, 7.93; N 6.17, 6.28. $C_{16}H_{17}N$. Calculated %: C 86.06; H 7.63; N 6.27.

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*In the cited source [9] n_D^{20} 1.4704 is given. This value is taken from the work of Kenyon and co-workers [10] and is clearly erroneous; it relates to a doubtful substance whose analysis for carbon differs from the theoretical by 0.7%.

**The value $[\alpha]_D^{20}$ + 21.6° refers not to the aqueous solution, as is incorrectly stated in work [2], but to a solution in 1 N hydrochloric acid, for which we obtained $[\alpha]_D^{17}$ + 21.4°, whereas Leithe [4] gives the value $[\alpha]_D^{15}$ + 20.8° (1 N hydrochloric acid, c 7.8).

***This batch of (−) (II) was used also for the preparation of other Schiff bases, besides salicylal-p-bromobenzal-, p-dimethylaminobenzal-, and furfural derivatives.

p-Toluylal-(−)-α-benzylethylamine

p-$CH_3-C_6H_4CH=N-CH(CH_3)CH_2C_6H_5$ was prepared like the preceding from 3.8 g of (−) (II) and 3.16 ml of p-tolualdehyde; yield 3.45 g (52%).

B.p. 158-159° (3 mm), d_4^{20} 0.9897, n_D^{20} 1.5712, MR_D 78.8; calc. 76.5. $[\alpha]_D^{19}$ − 176° (benzene, c 1.9) − 217° (methanol, c 1.9) − 183.5° (acetone, c 2.2), − 159° (dichloroethane, c 2.2), − 262° (heptane, c 1.1).

Found %: N 5.80, 6.03. $C_{17}H_{19}N$. Calculated %: N 5.90.

p-Methoxybenzal-(−)-α-benzylethylamine

p-$CH_3OC_6H_4CH=NCH(CH_3)CH_2C_6H_5$ was prepared like the preceding from 5.07 g of (−) (II) and 5.10 g of anisaldehyde; yield 7.29 g (72%).

B.p. 167-170° (3 mm), d_4^{20} 1.047, n_D^{20} 1.5818, MR_D 80.7; calc. 78.2. $[\alpha]_D^{19}$ − 197° (benzene, c 1.8), − 227° (methanol, c 2.3), − 194° (acetone, c 2.0), − 176° (dichloroethane, c 1.6), − 191° (heptane, c 1.7).

Found %: N 6.04, 6.16. $C_{17}H_{19}ON$. Calculated %: N 5.53.

p-Nitrobenzal-(−)-α-benzylethylamine

p-$O_2NC_6H_4CH=N-CH(CH_3)CH_2C_6H_5$ was prepared like the preceding from 2.46 g of (−) (II) and 2.75 g of p-nitrobenzaldehyde in 30 ml of methanol. After the methanol was evaporated, the reaction product was isolated in solid form, m.p. 67-72° (unsharp because the substance was not optically pure).

$[\alpha]_D^{19}$ − 213° (benzene, c 2.3), − 214° (methanol, c 2.1), − 200° (acetone, c 2.4), − 186° (dichloroethane, c 1.5), − 199° (heptane, c 1.8).

Found %: N 10.26, 10.11. $C_{16}H_{16}O_2N_2$. Calculated %: N 10.44.

p-Dimethylaminobenzal-(+)-α-benzylethylamine

p-$(CH_3)_2N-C_6H_4-CH=N-CH(CH_3)CH_2C_6H_5$. Prepared like the preceding from 5.1 g of (+) (II), $[\alpha]_D^{20}$ + 19.2° (optical purity 53%), and 5.7 g of p-dimethylaminobenzaldehyde in 30 ml of benzene; yield 7.6 g (74%).

B.p. 216-219° (5 mm), m.p. 48-53°. $[\alpha]_D^{18}$ + 170° (benzene, c 2.1), + 170° (methanol, c 1.9), + 147° (acetone, c 2.3), + 128° (dichloroethane, c 1.4), + 177° (heptane, c 2.0).

Found %: N 10.56, 10.66. $C_{18}H_{22}N_2$. Calculated %: N 10.52.

Salicylal-(+)-α-benzylethylamine

o-$HOC_6H_4-CH=N-CH(CH_3)CH_2C_6H_5$ was prepared like the preceding from 2.8 g of (+) (II) (optical purity 75%) and 2.55 g of salicylaldehyde in 10 ml of methanol; yield 2.45 g (49.5%).

B.p. 164-168° (2 mm), m.p. 47-54° (unsharp owing to incomplete optical purity). $[\alpha]_D^{20}$ + 269° (benzene, c 2.1), + 347° (methanol, c 2.4), + 252° (acetone, c 1.9), + 237° (dichloroethane, c 2.5), + 274° (heptane, c 1.6).

Found %: N 5.95, 6.05. $C_{16}H_{17}ON$. Calculated %: N 5.85.

p-Bromobenzal-(+)-α-benzylethylamine

p-$BrC_6H_4CH=N-CH(CH_3)CH_2C_6H_5$ was prepared like the preceding from 0.59 g of (+) (II) (optical purity 100%) and 0.80 g of p-bromobenzaldehyde in 20 ml of methanol; it was purified by recrystallization from aqueous alcohol; yield nearly quantitative, m.p. 65°.

$[\alpha]_D^{20}$ + 243° (benzene, c 1.6), + 264° (methanol, c 1.3), + 240° (acetone, c 1.8) + 221° (dichloroethane, c 1.6), + 252° (heptane, c 1.3).

Found %: N 4.40, 4.57. $C_{16}H_{16}NBr$. Calculated %: N 4.64.

SUMMARY

1. α-Benzylethylamine has been resolved into optical antipodes by means of (−) menthyl hydrogen sulfate.

2. Schiff bases have been prepared from optically active α-benzylethylamine and aromatic aldehydes. Their optical activity in benzene, methanol, acetone, dichloroethane, and heptane has been determined.

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INVESTIGATIONS IN THE FIELD OF ORGANOCYCLOSILOXANES

IV. REACTIVITY OF ORGANOCYCLOSILOXANES IN DEPENDENCE ON THE NUMBER OF LINKS IN THE CYCLE

N. N. Sokolov

There is practically no information in the literature on the reactivity of cyclic organosilicon compounds. The mechanism of polymerization of organocyclosiloxanes by acid [1, 2] and basic [2-4] catalysts was studied only in application to reactions of rearrangement of linear and cyclic hydrolysis products of the monomers. A qualitative conclusion has been reached, on the more rapid polymerization of hexamethylcyclotrisiloxane in comparison with octamethylcyclotetrasiloxane. This effect is explained by the strain in the trimer ring [1].

The small amount of trimer in the hydrolysis products of dimethyldichlorosilane [5] also indicates the strain in this ring in comparison with higher ones. This conclusion is contradicted by the presence of a large amount of trimers in the hydrolysis products of diethyldichlorosilane [6] and the products of thermal re-forming of polydimethylsiloxanes [5].

A report [7] on the varying reactivity of dibutoxycyclosiloxanes should be noted: the trimer was 92% hydrolyzed by boiling water after 72 hours and the tetramer, 39%; after 48 hours the pentamer was 5% hydrolyzed and the hexamer, 3%. An open-chain compound, hexabutoxydisilane, was 5% hydrolyzed after 72 hours.

For the experiments we took cyclic compounds having a varying number of Si—O links in the ring and various radicals (substitutents) attached to the silicon.

Since hydrogen in compounds containing a Si—H bond reacts with alkalis, concentrated sulfuric acid (d 1.83) was used as polymerization catalyst, in the amount of 0.4 g for each 1/30 mole of the cyclic compound.

The rate of polymerization of cyclic compounds containing a Si—H bond, as preliminary experiments showed, was very high in comparison with that of cyclic compounds containing alkyl radicals and was moderated by using solvents. As in the case of polymerization of organic monomers, the polymerization rate, characterized by the change in the relative viscosity (η) of a 10% solution in benzene, increases as the dipole moment of the solvent increases (Table 1).

In the experiments benzene was used as a solvent. At a 50% concentration of the compounds being investigated the reaction rate is still quite high and can be measured, whereas at 30% concentration the reaction practically does not occur. The relative viscosity of the solution proved to be a linear function of the percentage (up to 4%) of catalyst for constant reaction time.

It should be noted that after a certain degree of polymerization (η = 3-5) is attained, a decrease of viscosity is observed in all cases. This effect is due to cessation of chain growth and to destruction of the already-formed polymer under the influence of the catalyst, as a result of which equilibrium is attained in the polymerized system. The given process takes place especially vigorously in solvents. On determining the viscosity of a 10% solution after the viscosity maximum is reached in a viscometer, a gradual decrease of viscosity is observed. In Fig. 1 are given the results of determination of η for a solution of 1 g of dimethylpolysiloxane rubber in 49 g of toluene or chlorobenzene in the presence of 4% of sulfuric acid. Under the same conditions, but without catalyst, no decrease of viscosity is observed.

TABLE 1

Effect of the Dipole Moment of the Solvent on the Rate of Polymerization of Triethylcyclotrisiloxane

Solvent	$\mu \cdot 10^{18}$	η after 20 minutes
Benzene	0	1.73
n-Heptane	0	1.85
Carbon tetrachloride	0	1.70
Toluene	0.4	2.07
Chlorobenzene	1.7	2.76
Nitrobenzene	4.0	5.0

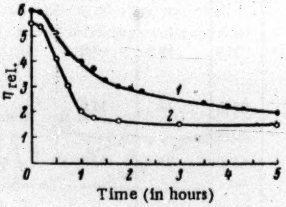

Fig. 1. Effect of solvents on the depolymerization of polydimethylsiloxane. 1) Toluene; 2) chlorobenzene.

In Figs. 2 and 3 is shown the kinetics of polymerization of organocyclosiloxanes containing a Si—H bond and without this bond (hexamethylcyclotrisiloxane measured in benzene), respectively.

In order to compare the rates of polymerization with and without solvent, triethylcyclotrisiloxane and tetraethylcyclotetrasiloxane were polymerized without benzene. It was found that 1:1 dilution with benzene increases time of the attainment of $\eta = 2.0$ sixtyfold. Proceeding from this transition coefficient, the time τ (in seconds) of polymerization of organocyclosiloxanes to $\eta = 2.0$, τ_{corr}, corrected by means of the coefficient, and the time τ_0, which is assumed to be equal to 1 for tetramethylcyclotetrasiloxane, are given in Table 2.

It follows from the experimental results, that as the number of links in rings with identical radicals increases, the time of polymerization to $\eta = 2$ increases. However, this increase is slight and apparently tends toward some limit. Thus, in the series $[\underset{\substack{|\\ \mathrm{H}}}{\mathrm{CH_3SiO}}]_{4-6}$ the ratio of the polymerization time τ_0 of the pentamer to that of the tetramer is 1.47, whereas the corresponding ratio for the hexamer and pentamer is 1.22. In the series $[(CH_3)_2SiO]_{4-6}$ the corresponding ratio for the pentamer and tetramer is 2.36, and that for the hexamer and pentamer is 1.86.*

The trimers all differ sharply in reactivity. Trimethylcyclotrisiloxane polymerizes rapidly (with decomposition), hexamethylcyclotrisiloxane polymerizes 351 times as quickly as octamethylcyclotetrasiloxane, etc.

The decisive role in determining polymerizability is played by the size of the radicals (substituents) attached to the silicon. As the radical becomes larger, the polymerization rate decreases. Thus the ratio of the polymerization times of tetramers with the substituents CH_3-H, C_2H_5-H, CH_3-CH_3, $C_2H_5-C_2H_5$ is equal to 1:11:586:10,286.

The effect of ring size on reactivity has been confirmed by us in the case of the cyclic series $[\underset{\substack{|\\ \mathrm{H}}}{\mathrm{CH_3SiO}}]_{3-6}$.

The oxidizability and reducing action of silanes are well known. Reactions of replacement of hydrogen in the Si—H bond in organo-substituted silanes also have been studied [8, 9].

In the study of the reactions of methylcyclosiloxanes with various reagents we found that trimethylcyclotrisiloxane is exceptionally nucleophilic. In contrast to higher cyclic compounds of the given series the trimer reduces Fe^{+++} to Fe^{++}, Cu^{++} to Cu, and Ag^{+} to Ag within a few minutes. Conc. HNO_3 is reduced by the trimer with evolution of NO_2 and formation of SiO_2 within 1 minute; in the case of the tetramer this process takes 40 minutes; in that of the pentamer, ~ 3 hours; in that of the hexamer, 4-15 hours. It is generally known that conc. H_2SO_4 does not react even with silanes, but acts as a catalyst in the polymerization of organocyclosiloxanes containing a Si—H bond. However, it was found that trimethylcyclotrisiloxane vigorously reduces sulfuric acid with rapid evolution of SO_2, which is not produced by higher cyclic compounds of this series or open-chain compounds under the same conditions.

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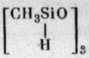
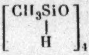
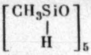
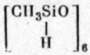
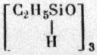
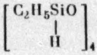
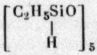
*We adhere to the established terminology, according to which the Si—O link is a member of the ring in organocyclosiloxanes.

TABLE 2

Rate of Polymerization of Organocyclosiloxanes

Cyclosiloxanes	Formula	Polymerization time (in sec)		τ_0
		τ in expt.	τ_{corr}	
Trimethylcyclotrisiloxane	 $\left[\underset{\substack{\mid\\ H}}{CH_3SiO}\right]_3$	< 1 with dec.	≪1	≪1
Tetramethylcyclotetrasiloxane	 $\left[\underset{\substack{\mid\\ H}}{CH_3SiO}\right]_4$	252	4.2	1
Pentamethylcyclopentasiloxane	 $\left[\underset{\substack{\mid\\ H}}{CH_3SiO}\right]_5$	374	6.2	1.47
Hexamethylcyclohexasiloxane	 $\left[\underset{\substack{\mid\\ H}}{CH_3SiO}\right]_6$	456	7.6	1.81
Triethylcyclotrisiloxane	 $\left[\underset{\substack{\mid\\ H}}{C_2H_5SiO}\right]_3$	758	12.6	3.0
Tetraethylcyclotetrasiloxane	 $\left[\underset{\substack{\mid\\ H}}{C_2H_5SiO}\right]_4$	2760	46	11.0
Pentaethylcyclopentasiloxane	 $\left[\underset{\substack{\mid\\ H}}{C_2H_5SiO}\right]_5$	4500	75	17.8
Hexamethylcyclotrisiloxane	$[(CH_3)_2SiO]_3$	420	7	1.66
Octamethylcyclotetrasiloxane	$[(CH_3)_2SiO]_4$	2460	2460	586
Decamethylcyclopentasiloxane	$[(CH_3)_2SiO]_5$	5820	5820	1386
Dodecamethylcyclohexasiloxane	$[(CH_3)_2SiO]_6$	10800	10800	2570
Hexaethylcyclotrisiloxane	$[(C_2H_5)_2SiO]_3$	23400	23400	5570
Octaethylcyclotetrasiloxane	$[(C_2H_5)_2SiO]_4$	43200	43200	10286

Turning to the experience of organic chemistry, we find that the Baeyer-Sachse-Mohr theory made it possible to relate ring strain in cyclic compounds generally to their reactivity. Carothers further concluded that the stability of cyclic compounds depends on the size of the ring, increasing as the latter increases [10]. Correlations between ring size and reactivity were found for cycloalkane derivatives [11]. On the basis of the ability of cycloolefins to form complexes with silver, it was established [12] that the degree of strain, with regard to which cyclopentane ≥ cycloheptane > cyclohexane, corresponds to the reactivity; in this case, the electron-donor properties of the cyclic compounds are enhanced as the strain increases. Strepikheev and Skuratov [13] determined the heats of combustion of certain lactams, as well as their strain, and found that a high degree of ring strain corresponds to a high rate of polymerization. They noted that the reactivity of heterocyclic compounds of the same ring structure depends on the structure of the substituents.

Korshak [14], on generalizing the voluminous experimental data, reached the conclusion that the polymerizability of heterocyclic compounds accords in the main with the strain theory. Three-membered rings polymerize most readily. The screening effect of substituents is very important.

In organocyclosiloxanes a great degree of strain in the trimers must be assumed. Actually a Si—O—Si bond angle of 160 ± 15° was found in open-chain polymethylsiloxanes [15], whereas the O—Si—O bond angle is near 109° 28'. The oxygen bond angle in polyethylsiloxanes was found to be 168° [16]. In disiloxane $H_3SiOSiH_3$ this angle is assumed to be almost linear (180°) [17]. Flory [18] thinks that the most probable value of the oxygen bond angle is 145°. From these data it must be concluded that considerable strain is present in the cyclic trimers. It was found [19] that hexamethylcyclotrisiloxane has a strained planar structure, while the strain in octamethylcyclotetrasiloxane is mitigated by the nonplanar configuration of the ring. Obviously a nonplanar configuration must be assumed also for the higher organocyclosiloxanes.

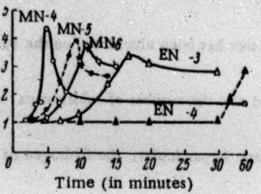


Fig. 2. Kinetics of polymerization of methyl- and ethylcyclosiloxanes containing a Si—H bond. MN-4) Tetramethylcyclotetrasiloxane; MN-5) pentamethylcyclopentasiloxane; MN-6) hexamethylcyclohexasiloxane; EN-3) triethylcyclotrisiloxane; EN-4) tetraethylcyclotetrasiloxane.

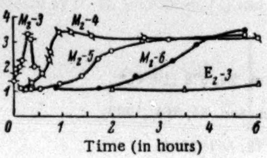


Fig. 3. Kinetics of polymerization of dimethyl- and diethylcyclosiloxanes. M_2-3) Hexamethylcyclotrisiloxane; M_2-4) octamethylcyclotetrasiloxane; M_2-5) decamethylcyclopentasiloxane; M_2-6) dodecamethylcyclohexasiloxane; E_2-3) hexaethylcyclotrisiloxane.

EXPERIMENTAL

The polymerization experiments were performed in a 90 ml, round-bottom flask provided with necks for a reflux condenser and a mercury-seal stirrer, for a thermometer, and for sampling. The stirrer was driven by a constant-current motor with a reducing gear and had a constant rate of 315 rpm. The lower end of the stirrer was set at a fixed distance of 1 mm from the bottom of the flask. The temperature was maintained at 21 ± 0.1° by a water thermostat. Organocyclosiloxanes not containing a Si—H bond were taken in 20 g quantities; sulfuric acid was taken at a rate of 0.4 g per 1/30 mole of the substance being polymerized. Thus, for instance, 0.81 g of sulfuric acid was taken for octamethylcyclotetrasiloxane (M 296, 1/30 M = 9.9). Samples were weighed into a prepared tare and immediately dissolved in about half the amount of benzene in order to arrest polymerization. This operation took not more than 1 minute. Then the required weight of benzene was added.

Organocyclosiloxanes containing a Si—H bond were taken in the amount of 5 g + 5 g of benzene. The catalyst was introduced in the amount previously calculated for 5 g of the organocyclosiloxane. Because of the rapid course of the reaction with cyclic compounds of this group, no samples were taken during the reaction. Each experiment was performed separately during a set time. At the end of the set time 40 g of benzene was added all at once to the reaction mixture in the flask, with the stirrer running. This stopped the reaction, and a solution ready for viscosity measurement was obtained.

All experiments were performed under strictly identical conditions, since the polymerization rate, according to preliminary data, is considerably affected by the experimental conditions — the shape of the vessel, stirring rate, volume of the liquid phase, etc.

The procedure and apparatus adopted, as control experiments showed, provides good reproducibility of results.

For control, experiments on the polymerization of certain organocyclosiloxanes were performed with the same quantity of catalyst. It was found that the variation in the amount of catalyst, resulting from its calculation on the basis of the molecular weight of one or another organocyclosiloxane, cannot have any substantial effect on the results of the experiments. Thus η for tetraethylcyclotetrasiloxane with 0.27 g of sulfuric acid after 17 minutes was equal to 1.04, while η for triethylcyclotrisiloxane with the same quantity of sulfuric acid after 17 minutes was 3.4; η for decamethylcyclopentasiloxane with 0.81 g of sulfuric acid after 1 hour was 1.6, while η for octamethylcyclotetrasiloxane with the same amount of catalyst after the same time reached 3.4.

To compare the polymerization rates with and without solvent, 20 g of tetraethylcyclotetrasiloxane with 0.816 g of catalyst was polymerized without benzene, η = 2.0 being reached after 45 seconds. In the experiment with benzene the same viscosity was reached after 46 minutes. In the case of triethylcyclotrisiloxane η = 2.0 was obtained after 11 seconds and 12 minutes 32 seconds, respectively. From this a transition coefficient of 60 (within the limits of experimental error) was derived.

The effect of solvents on the polymerization rate was studied in the case of triethylcyclotrisiloxane. Five g of the latter (+ 0.27 g of sulfuric acid) and 0.064 mole of solvent were taken. The duration of the experiment at 20° was 20 minutes, after which the entire reaction solution was diluted with benzene to 10% concentration and the viscosity was determined.

SUMMARY

1. The dependence of the reactivity of organocyclosiloxanes on ring size has been elucidated on the basis of a study of polymerization reactions and reducing action.

2. It has been established that as the number of links in the rings, and also the number of substituents attached to the silicon, increases, the polymerizability decreases.

3. Cyclic trimers display enhanced reactivity, trimethylcyclotrisiloxane in particular; the hydrogen of the Si—H bond in the latter has pronounced electron-donor properties.

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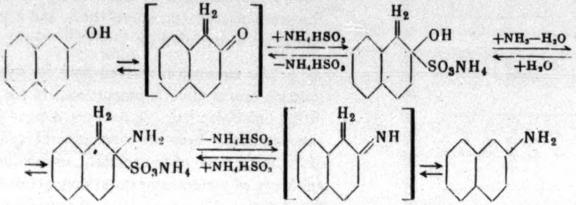
**In Russian.

INVESTIGATIONS IN THE NAPHTHALENE SERIES

XVIII. ON THE KINETICS OF INTERACTION OF β-NAPHTHOL WITH AQUEOUS SOLUTIONS OF AMMONIA AND AMMONIUM SULFITE*

V. V. Kozlov and I. K. Veselovskaia

The amination of naphthols by aqueous solutions of ammonia in the presence of sulfites is of great practical importance in the preparation of naphthylamines. The chemism of this interaction is explained by the scheme proposed by N. N. Vorozhtsov [1] and is interpreted by us in the following form:



(1)

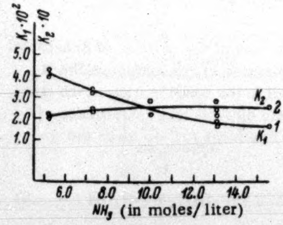


Fig. 1. Dependence of the rate constant for the amination of β-naphthol on the ammonia concentration.

Naphthol may react with sulfites both in the keto form, in which it has not yet been possible to isolate it [2], and in the enol form, which gives an addition product corresponding to the keto form. The kinetic aspect of this process has not been described, either.

Below we set forth the results of a study of the kinetics of interaction of β-naphthol (m.p. 122°) with aqueous ammonia in the presence of ammonium sulfite.

The aqueous ammonia solution was prepared by saturating distilled water with ammonia gas (the concentration of the solutions was determined by titration with 0.5 N sulfuric acid).

Crystalline ammonium sulfite was prepared by saturating a 35% aqueous ammonia solution with sulfur dioxide gas. The $(NH_4)_2SO_3$ concentration was determined iodometrically before each experiment.

The amination was carried out in a rotary steel autoclave of 245 ml capacity which was wrapped in asbestos and uniformly heated by a gas-burner flame. The temperature within the autoclave did not vary more than ± 0.5° during the experiment. The heating of the contents of the autoclave to 150-180° lasted 15-16 minutes. At the end of the stated time the autoclave was cooled with cold water to 70°. After 30 minutes the completely cooled autoclave was opened for emptying.

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*For paper XVII see: JGC 27, 3041 (1957) [See C.B. Translation].

TABLE 1

Dependence of the Reaction Rate on the Ammonia Concentration

Concentration of NH_4 (in %)	27.5		24.53		18.3		13.27		9.22	
C_a	15.58		13.10		9.96		7.34		5.21	
C_s	0.350	0.350	0.350	0.38	0.353	0.350	0.349	0.350	0.350	0.380
a (in %)	70.80	70.80	61.0	65.4	62.5	55.1	51.0	50.3	38.1	41.1
Temperature	159.8°	160.1°	160.2°	160.0°	160.0°	160.2°	159.8°	160.0°	159.7°	160.0°
$K_1 \cdot 10^2$	1.64	1.64	2.17	1.87	2.22	2.84	3.22	3.26	4.23	3.91
$K_2 \cdot 10$	2.55	2.55	2.84	2.45	2.21	2.83	2.36	2.40	2.21	2.04

Note: Experimental conditions: 5.505 g of β-naphthol, 6.00 g of $(NH_4)_2SO_3$, 100 ml of ammonia (9-27%), 160°, 60 minutes.

The contents of the autoclave were quantitatively transferred with the aid of water to a vessel, and the precipitate which was present in the mixture was filtered off and washed with 5% sodium hydroxide solution until the wash waters ceased to give a test for β-naphthol. The unreacted β-naphthol in the combined solution of mother liquor and wash waters was determined by adding 50 ml of the solution to a 0.1 N solution of a benzenediazonium salt in a soda medium. The amount of ammonia in the experiments corresponded to 13-40 moles per mole of β-naphthol, which assured a practically constant ammonia concentration and the presence of β-naphthol in the solution during the high-temperature reaction.

The rate constant of the reaction of β-naphthol with ammonia in the presence of ammonium sulfite was originally calculated according to Eq. (2), where

$$K_1 = \frac{2.303}{t \cdot C_s} \cdot \lg \frac{100}{a}, \qquad (2)$$

t is the reaction time in minutes, C_s is the ammonium sulfite concentration (in moles/liter), and a is the quantity of unreacted β-naphthol (in % of that taken).

This equation is derived from the hypothesis that the reaction rate is directly proportional to the β-naphthol and sulfite concentrations and does not depend on the ammonia concentration. From the experimental results of the study of the interaction of β-naphthol, ammonium sulfite, and ammonia of various concentrations, given in Table 1 and Fig. 1 (Curve 1), the variation of the reaction rate constant may be determined in the range from $1.64 \cdot 10^{-2}$ to $4.07 \cdot 10^{-2}$ moles/liter/minute.

Assuming that the rate of the reaction of β-naphthol with ammonia in the presence of ammonium sulfite is directly proportional not to the concentration of the latter, but to that of ammonium bisulfite as a consequence of dissociation according to scheme (3), we made the appropriate calculations.

$$(NH_4)_2SO_3 + HOH \rightleftarrows NH_4HSO_3 + NH_4OH \qquad (3)$$

On the basis of the relation

$$\frac{[NH_4HSO_3][NH_4OH]}{[(NH_4)_2SO_3]} = K_{\text{hydr.}} \qquad (4)$$

the ammonium bisulfite concentration may be expressed by the equation

$$C_{\text{bs}} = K_{\text{hydr.}} \frac{C_s}{C_a}, \qquad (5)$$

where: C_{bs} is the ammonium bisulfite concentration, C_s is the ammonium sulfite concentration, and C_a is the ammonia concentration.

TABLE 2

Dependence of the Reaction Rate Constant on the β-Naphthol Concentration

$C_{10}H_7OH$ (in g)	2.736		5.472		8.208	
a (in %)	64.2	61.4	69.4	65.4	66.9	61.7
Temperature	160.0°	160.0°	160.0°	160.0°	160.2°	160.4°
$K_2 \cdot 10$	2.52	2.79	2.15	2.45	2.29	2.75

Note: Experimental conditions: 100 ml of 24.2 % ammonia, 6.30 g of $(NH_4)_2SO_3$, 160°, 60 minutes.

TABLE 3

Dependence of the Reaction Rate Constant on the Amount of Ammonium Sulfite

$(NH_4)_2SO_3$ (in g)	2.84		3.88		8.14
C_S	0.163		0.223		0.463
C_a	13.20		12.44		12.44
a (in %)	85.0	85.0	74.6	73.4	52.8
Temperature	160.2°	159.9°	159.6°	159.6°	160.5°
$K_2 \cdot 10$	2.20	2.20	2.72	2.87	2.82

Note: Experimental conditions: 5.505 g of β-naphthol, 100 ml of 24.3% ammonia, 160°, 60 minutes.

TABLE 4

Dependence of the Reaction Rate Constant on Time

Duration of experiment (in minutes)	90		120		150	
C_S	0.360	0.380	0.360	0.297	0.352	0.285
a (in %)	49.0	54.5	38.7	54.5	36.7	51.1
Temperature	159.8°	160.7°	160.0°	159.9°	160.1°	160.0°
$K_2 \cdot 10$	2.88	2.33	2.88	2.23	2.49	2.06
Naphthylamine (in %)	40.6		—		58.8	

Note: Experimental conditions: 5.505 g of β-naphthol, 100 ml of 24.5% ammonia, 160°.

The practical invariance of the rate constant (K_2), calculated according to Eq. (6)

$$K_2 = \frac{2.303 \cdot C_a}{t \cdot c_S} \lg \frac{100}{a} \tag{6}$$

and given in Table 1 and Fig. 1 (Curve 2), shows that the reaction rate actually is directly proportional to the bisulfite concentration.

From the data of Tables 2-4 on determination of the dependence of the rate constant on the β-naphthol

TABLE 5

Dependence of the Reaction Rate Constant on Temperature

Temperature	150.4	149.4	150.0	160.0	159.6	160.2	160.0	169.6	170.0	170.2	180.7	180.2
C_S	0.380	0.380	0.380	0.372	0.380	0.380	0.380	0.361	0.304	0.300	0.361	0.300
a (in %)	80.1	79.5	82.8	69.4	65.4	61.0	65.4	44.8	47.7	47.7	34.7	43.6
K_2 exptl.	0.128	0.132	0.109	0.215	0.245	0.284	0.245	0.485	0.532	0.538	0.640	0.607
K_2 exptl.av.		0.120			0.247				0.518		0.623	
K_2 calcd.		0.118			0.249				0.512		1.018	

Note: Experimental conditions: 5.505 g of β-naphthol, 6.00 g of $(NH_4)_2SO_3$, 100 ml of 24.5% ammonia, 60 minutes.

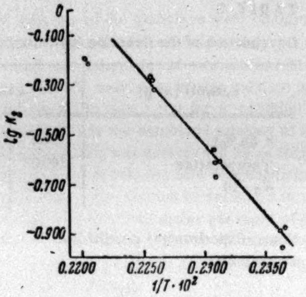

Fig. 2. Dependence of the rate constant of the amination of β-naphthol on temperature.

concentration, the amount of ammonium sulfite taken, and the duration of the experiment, it can be established that the value of the reaction rate constant (K_2), calculated according to Eq. (6), is practically invariant. (The variation in the value of the reaction rate constant in dependence on the amount of the charge in the autoclave, as calculations showed, lies within acceptable limits).

In a work on the amination of 1,5- and 1,4-naphtholsulfonic acids Cowdrey [3] gives a scheme in which he assumes that the HSO_3^- ion takes part in the reaction. Furthermore, in the corresponding calculations he does not take into account the degree of dissociation of the different sulfites, but states that the rate of the amination reaction depends on the concentration of $SO_3^=$ ions and bound NH_4, thereby making an obvious error.

The reaction rate constants at various temperatures are given in Table 5.

The dependence of lg K_2 on the inverse temperature is shown in the form of a straight line in Fig. 2. Experimental values of log K_2, in accordance with the Arrhenius equation, fit the straight line well.

From the data of Table 5 the calculated activation energy of the reaction of β-naphthol with aqueous ammonia in the presence of ammonium sulfite is equal to 27,300 cal/mole.

The dependence of the reaction rate constant on temperature may be represented by the equation:

$$\lg K_2 = 13.219 - \frac{5984.8}{T} \pm 0.008. \qquad (7)$$

Values of the constant, calculated by this equation, are given in the last line of Table 5 and agree fully with the experimentally determined constants. Constants found in experiments at 180° are somewhat diminished owing to a change in the sulfite concentration, caused by slight corrosion observed in the autoclave. The cause of the latter was an increase in the NH_4HSO_3 concentration, due to the great degree of dissociation of $(NH_4)_2SO_3$, occurring at high temperature with appreciable transition of ammonia to the gas phase. As is evident from the data of Table 1, an increase in the ammonia concentration leads to a decrease in the amount of naphthol entering into the reaction, probably owing to a decrease in the dissociation of ammonium sulfite according to scheme (3).

The completeness and character of the hydrolysis of the different sulfites, and hence the effect of hydrolysis on the completeness of the amination of naphthol, are evident from the following results, which were obtained by us in the reaction of aqueous ammonia and β-naphthol for 6 hours at 180°; in the presence of ammonium sulfite the percentage of conversion was 94, in that of sodium ammonium sulfite it was 88, and in that of sodium sulfite it was 40.

Thus the data set forth fully confirm reaction scheme (1) for amination.

We shall return to the doubts, expressed by Cowdrey [4] regarding the need for formation of an addition product through preliminary ketonization, in a separate paper.

The rate of the entire amination process is determined by the rate of its first phase, i.e., the rate of the reaction of β-naphthol with bisulfite (NH_4HSO_3 or $NaHSO_3$). The addition product of scheme (1) is extremely reactive, and therefore it reacts further with ammonia to form naphthylamine at a rapid rate, greatly exceeding the rate of its formation. The rate of conversion of β-naphthol depends on time and temperature, being directly proportional to the product of the concentrations of naphthol and bisulfite, and does not depend on the ammonia concentration. The rate of amination may be expressed also as a function of the concentration of ammonium sulfite in the charge. In this case the reaction rate is directly proportional to the product of the concentrations of β-naphthol and sulfite and inversely proportional to the ammonia concentration.

SUMMARY

The kinetics of amination of β-naphthol has been studied, and the reaction scheme first proposed by N. N. Vorozhtsov has been fully confirmed.

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SYNTHESIS OF CERTAIN DERIVATIVES OF ADRENALIN

II. D,L-ADRENOCHROME OXIME AND SEMICARBAZONE

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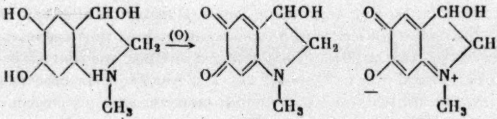
Among the oxidation products of L-adrenalin (I), that having the greatest theoretical and practical interest is the so-called adrenochrome, which is customarily represented by structural formula (II) [1].



(I) (II) (III)

However, formula (II) is not in accord with the actual properties of this compound in which, for instance, only the carbonyl group can be found, since in contrast to other o-quinones it gives only monocarbonyl derivatives (monooxime, monosemicarbazone, monohydrazones). Its other chemical and physicochemical properties (color, solubility, etc.) do not correspond to structure (II), either. On this basis Harley-Mason [2] proposed for it the structure of zwitterion (III), which differs from (II) only in the disposition of the double bonds, so that the question here is that of the density distribution of the electron cloud.

Owing to its interesting physiological properties, L-adrenochrome has attracted a great deal of attention from pharmacologists [3], the very unstable quinone proving to be replaceable for pharmacological purposes by its completely stable monocarbonyl derivatives, the monooxime and monosemicarbazone. Of these, the latter, widely known in the foreign literature under the name "adrenoxyl," proved to be the more interesting.

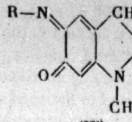
The preparation of the oxime and especially the semicarbazone from L-adrenochrome has been described many times, the published directions being very similar [1, 5-9]. The yield of the semicarbazone, according to literature data, does not exceed 40%, based on adrenochrome, the yield of which, in turn, scarcely comes to 50%, based on adrenalin. Data on the yield of the oxime are lacking. The preparation of certain derivatives of adrenochrome directly from adrenalin, which was oxidized in aqueous solution, is also described [10, 11].

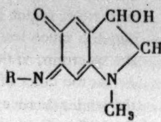
In the present paper a description of the synthesis of the monooxime and monosemicarbazone of racemic adrenochrome and the results of an investigation of some of their properties are given. Neither of them has been examined pharmacologically to any appreciable extent [4], and no data on their synthesis and properties have been published.

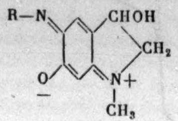
We oxidized D,L-adrenalin in an aqueous medium with potassium ferricyanide [12], after which semicarbazide or hydroxylamine was added to the resulting solution of adrenochrome, and the corresponding monoderivative was isolated in 80% yield for the semicarbazone and 50% yield for the oxime.

Analysis of the properties of adrenochrome monooxime and monosemicarbazone permits certain conclusions to be drawn regarding the details of their structure, which has scarcely been discussed as yet, although the problem of structure is not solved. After the present work was finished, a paper appeared [13], containing new data relating to the structure of the semicarbazone, which agree in part with those obtained by us. Both the oxime and the semicarbazone of adrenochrome might be obtained in the form of the two nontautomeric isomers (IV) and (V).

On the basis of their properties it is not possible to choose between these two formulas, but both are inacceptable, because the impossibility of obtaining dicarbonyl derivatives of adrenochrome cannot be explained on the basis of either. If the zwitterion structure with quaternary onium nitrogen (III), proposed by Harley-Mason [2], is assumed for adrenochrome, the problem of the structure of its carbonyl derivatives is simply solved; compound (III) can form only a monoderivative of structure (VI).


(IV)


(V)


(VI)

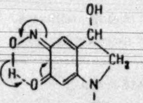
R=OH, NH_2CONH

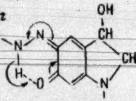
However, formula (VI) is at variance with a number of properties of the substances which it should represent. Primarily this regards the matter of their color. Solutions of adrenochrome in polar solvents (they are insoluble in nonpolar ones) have a cherry-red hue of high intensity, which may be explained, assuming that it has structure (III), by the presence of an ionized chromophore such as onium nitrogen attached to a quinoid ring by a double bond.* If the monooxime and monosemicarbazone had structure (VI), they would have to have a color of the same, or even greater, depth. Instead, a sharp hypsochromic effect is observed on their formation (both substances give orange-yellow solutions of no great intensity), which indicates a substantial difference between the electronic structures of the compounds being compared.

Certain chemical properties of the compounds being considered also are at variance with formula (VI). According to formula (VI) they must be zwitterions in which the cation is that of a strong quaternary ammonium base, and the anion is that of a weak, phenolic-type acid. The isoelectric point of such a zwitterion would have to lie in the alkaline region. However, potentiometric titration of adrenochrome monooxime and monosemicarbazone with alkali and acid in an aqueous medium showed that, although both are amphoteric, their basic properties are considerably weaker than their acid ones (Figs. 1 and 2). The fact that aqueous solutions of these compounds have not a basic, but rather an acid reaction is in accord with this. The apparent acid dissociation constants K_a, calculated from titration data, were found to be equal to $1.6 \cdot 10^{-11}$ ($pK_a = 10.8$) for the semicarbazone and $2.5 \cdot 10^{-9}$ ($pK_a = 8.6$) for the oxime. As regards the basic properties, they are so weak for both compounds that the corresponding constants could not be determined. Nevertheless, both substances could give fully characteristic, although not very stable, picrates, which were isolated by us and analyzed.

On the basis of their properties a structure similar to that of o-nitrophenol might be assumed for adrenochrome monooxime, whereas the structure of the monosemicarbazone might be considered to be like that of an o-oxyazo compound. With such a structure both of the compounds under consideration should be capable of forming an intramolecular hydrogen bond; this in turn should lead to a tendency to assume a benzoid structure instead of a quinoid one which apparently occurs in the original adrenochrome molecule.

This may be expressed in the form of formulas (VII) for the oxime and (VIII) for the semicarbazone.


(VII)


(VIII)

Both (VII) and (VIII) should give chelate complexes with metals. Actually, as we have established, both the monooxime and the monosemicarbazone of adrenochrome can give such complexes with the ions Co^{2+}, Ni^{2+}, Cr^{3+}, Fe^{3+} and Fe^{2+}. Compounds with bivalent iron have a grassy-green color, whereas the rest have a reddish-orange hue many times more intense than that of the original compound. The color of the cobalt complex is distinguished by its peculiar intensity.

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* The intense and deep color of aniline blue in polar solvents [14], for instance, is similarly explained.

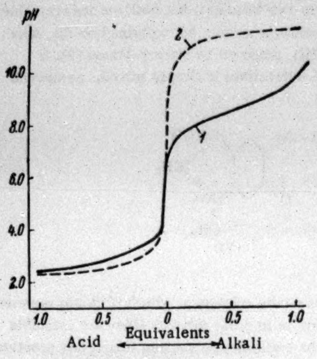


Fig. 1. Potentiometric titration curves. 1) Adrenochrome monooxime; 2) water.

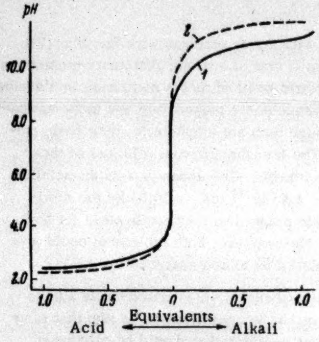
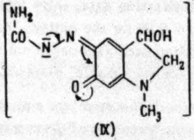
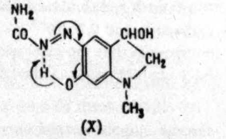


Fig. 2. Potentiometric titration curves. 1) Adrenochrome monosemicarbazone; 2) water.

Indirect arguments in favor of the above-stated hypothesis that the investigated compounds have structures (VII) and (VIII) were obtained on examination of their absorption spectra in neutral, acid, and alkaline media. In the spectrum of the neutral aqueous solution of the semicarbazone, two bands are readily distinguished (Fig. 3). One of them lies in the near ultraviolet region (λ_{max} = 3600 A, $\epsilon_{max} = 2 \cdot 10^4$); the other, which is much less intense, is located in the visible part of the spectrum, in the 4200-4700 A range ($\epsilon_{max} = 5 \cdot 10^3$), and causes the color of the solution. In an alkaline medium, where the semicarbazone is converted to the corresponding anion, the intense band is shifted from the ultraviolet to the visible region, its extinction increasing markedly (λ_{max} = 4450 A,* $\epsilon_{max} = 3.25 \cdot 10^4$). Changes of this kind in the absorption spectrum on ionization are characteristic of all phenols, as is generally known. It is customary to explain them by the enhancement of the electron-donor properties of the phenol oxygen on formation of the phenolate which for this reason acquires a tendency to assume the quinoid structure as a result of the displacement of electrons from the negatively charged oxygen to the benzene (and, in general, aromatic) ring.** If such an explanation is correct, the structure of the monosemicarbazone anion should be as shown in (IX), where the curved arrows indicate the direction of displacement of the electron cloud on delocalization of the negative charge of the ion, which undoubtedly must occur. The undissociated form of this compound, which absorbs in a shorter-wavelength region, would have to correspond to this to acquire structure (X).



(IX)



(X)

Under the influence of the positively charged nitrogen of the dihydroindole ring, in an acid medium, electrons are shifted toward the middle, six-membered ring, which thereby acquires a still more "benzenoid" character. This is easily observable on the absorption curve; the band in the long-wave part is smoothed out, but the absorption in the short-wave region increases. Similar conclusions may be drawn on interpretation of the absorption spectrum of adrenochrome monooxime (Fig. 4).

EXPERIMENTAL

D,L-Adrenochrome monosemicarbazone. A 2.75 g quantity (0.015 mole) of purified D,L-adrenalin [16] was dissolved in 30 ml of water and a sufficient amount of concentrated acetic acid (without excess). A solution of 19.5 g (0.06 mole) of potassium ferricyanide and 6.3 g (0.075 mole) of sodium bicarbonate in 80 ml of water was separately prepared, the first being dissolved on heating and the second being added in the cold. The prepared solution of oxidizing agent was added during 60-80 seconds to the vigorously stirred solution of adrenalin. The mixture immediately acquired an intense cherry-red hue and grew slightly warmer. After stirring for 5 minutes

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* According to literature data [13]., 4370 A.

** For example, see [15].

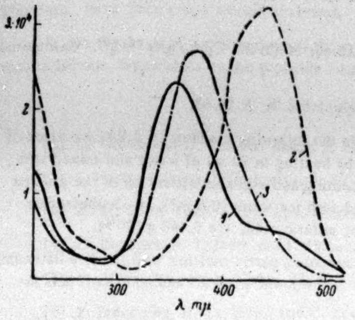

Fig. 3. Absorption spectrum of adrenochrome monosemicarbazone.
1) In water; 2) in 0.02 N NaOH; 3) in 0.08 N HCl.

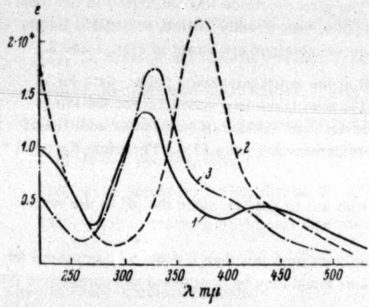

Fig. 4. Absorption spectrum of adrenochrome monooxime.
1) In water; 2) in 0.02 N NaOH; 3) in 0.08 N HCl.

a solution of 2.4 g (0.022 mole) of semicarbazide hydrochloride and 4.5 g of crystalline sodium acetate in 15 ml of water was added to it. To complete the reaction the liquid was stirred for 15 minutes at room temperature and then for 1.5-2 hours with cooling in an ice bath, after which the semicarbazone formed was filtered off, and washed in the filter with ice water until a pure orange-yellow filtrate was obtained. The precipitate, thoroughly pressed out on the filter, was then washed twice with an alcohol-ether (1 : 3) mixture and finally with pure ether. The yield of uncrystallized product with m.p. 218-220° (corr.) was 2.8 g (79%). After two crystallizations from water the compound melted with decomposition at 223° (corr.).

D,L-Adrenochrome monosemicarbazone is difficultly soluble in water (about 0.5 g in 1 liter at 20°), from which it crystallizes in the form of long, orange prisms with sharp edges, which do not contain solvent. It dissolves somewhat better in methanol, ethanol, or pyridine. Readily soluble in dilute alkali; soluble with more difficultly in dilute acid. It rapidly decomposes on heating in acid solution, turning brown .

Found %: N 23.77, 23.65. $C_{10}H_{12}O_3N_4$. Calculated %: N 23.72.

The picrate of the semicarbazone was obtained by mixing separately prepared hot solutions of 0.233 g of picric acid in 5 ml of water and 0.236 g of the semicarbazone in 20 ml of water (without striving for complete solution) and quickly filtering the still-hot mixture into a receiver placed in an ice bath, containing a small amount of the picrate for seed. The picrate formed was filtered off, washed on the filter with ice water (0.5 ml), an alcohol-ether mixture, (1 : 5), and ether. After drying in vacuo over sulfuric acid it had the form of a deep-yellow powder with a cryptocrystalline structure, which decomposes (partially melting) at a temperature near 150° and is difficultly soluble in water and readily soluble in methanol, ethanol, and acetone. On recrystallization from water it partly dissociates and is obtained in a mixture with the semicarbazone.

Found %: N 21.27, 21.18. $C_{16}H_{15}O_{10}N_7$. Calculated %: N 21.07.

D,L-Adrenochrome monooxime. To a solution of adrenochrome, prepared from 2.75 g of D,L-adrenalin (see above), was added a solution of 1.53 g (0.022 mole) of hydroxylamine hydrochloride and 4.5 g of crystalline sodium acetate in 15 ml of water. After stirring for 15 minutes at room temperature the mixture was left to stand for 1.5-2 hours in an ice bath, and the oxime formed was filtered off and washed with ice water until a light-orange filtrate was obtained, and then with an alcohol-ether mixture (1 : 5) and ether. The crude product was recrystallized twice from water and dried to constant weight at 100°. Yield 1.5-1.6 g (50-55%).

Racemic adrenochrome monooxime was isolated on recrystallization from water in the form of two crystal hydrates: short, deep-red prisms of the monohydrate, which separated out from hot, concentrated solutions, and long, thin, bright-orange needles of the dihydrate, which slowly separated out from cooled solutions. Both crystal hydrates were often obtained simultaneously. They have the same melting point, 178° (dec) (corr), and either is readily converted to the other on recrystallization.

Monohydrate. Found %: H_2O (by weight loss over P_2O_5) 8.50, 8.30; N 13.03, 13.48. $C_9H_{10}O_3N_2 \cdot H_2O$. Calculated %: H_2O 8.49; N 13.20.

Dihydrate. Found %: H_2O (by weight loss over P_2O_5) 15.63, 15.46; N 12.28. $C_9H_{10}O_3N_2 \cdot 2H_2O$. Calculated %: H_2O 15.64; N 12.17.

Anhydrous oxime. Found %: N 14.60, 14.55. $C_9H_{10}O_3N_2$. Calculated %: N 14.43.

The picrate of D,L-adrenochrome monooxime was obtained in the following manner. A 0.232 g portion of the oxime, twice recrystallized and dried over P_2O_5, was dissolved by heating in 20 ml of water and mixed with a hot solution of 0.28 g of picric acid in 7 ml of water. On rapid cooling and vigorous trituration of the oil first formed, precipitate was obtained, which was filtered off and washed with ice water (0.5 ml), an alcohol-ether mixture (1 : 5), and ether. The yield of picrate, dried in vacuo over sulfuric acid, was 0.406 g (80%).

The picrate of the oxime is a light-yellow powder which decomposes, partly melting with marked darkening, at a temperature near 124°. It dissolves poorly in water, but better in the lower alcohols and acetone; it is insoluble in benzene and ether.

Found %: N 16.50, 16.44. $C_{15}H_{13}O_{10}N_5$. Calculated %: N 16.55.

Potentiometric titration of D,L-adrenochrome monoxime and monosemicarbazone. Either 0.118 g (0.5 millimole) of the monosemicarbazone or 0.098 g of the monooxime of D,L-adrenochrome was dissolved in 100 ml of freshly boiled, redistilled water, and the cautiously cooled supersaturated solution was titrated by means of a 0.05 N solution of NaOH or HCl, at 20° with glass and calomel electrodes. The PL-5 vacuum-tube voltmeter (pH meter) of the GIPKh* system was used for emf measurement. The glass electrode was calibrated in the usual manner with standard buffer solutions. The same volume (100 ml) of solvent (freshly boiled, redistilled water) was similarly titrated with 0.05 N alkali and acid. The titration curves obtained are shown in Figs. 1 and 2.

The acid dissociation constants were calculated from the pH at the semiequivalence point; data for a blank which was run by titrating the same volume of pure water [17] were taken into account. For the semicarbazone, pH = 10.7 at the semiequivalence point. On titration of the same volume of water after addition of 0.5 equivalent of alkali (calculated for a sample of the titrated semicarbazone), pH = 11.4. Therefore $K_a = [H] = 10^{-10.7} - 10^{-11.4} = 1.6 \cdot 10^{-11}$ and $pK_a = 10.8$.

In the case of the monooxime the correction for water titration was negligible, since the pH at the semiequivalence point was 8.6, and $pK_a = 8.6$.

Since the measurements were performed in solutions with ionic strength less than 0.005, the corrections for ion activity did not exceed the experimental error, and the constants found may be considered to approximate the thermodynamic values.

Determination of the absorption spectra of D,L-adrenochrome monooxime and monosemicarbazone in aqueous solution. Three 2.5 ml portions of a 0.001 M solution of the compound were separately diluted to 50 ml with water, 0.02 N NaOH solution, and 0.08 N HCl solution. Light-absorption measurements were performed in the usual manner in the 2200-5400 A range with a SF-4 spectrophotometer. The absorption curves are shown in Figs. 3 and 4 for D,L-adrenochrome monosemicarbazone and monooxime, respectively.

Preparation of complex ions (lakes) of D,L-adrenochrome monooxime and monosemicarbazone with metal salts. To 5 ml of a 0.005 M solution of the monooxime or monosemicarbazone in a 0.1 M solution of sodium acetate (prepared by heating in a water bath) was added 0.5 ml of a 0.05 M solution of the appropriate metal salt. The mixture was kept at 45-50° for 20-30 minutes. In this case the original color of the orange-yellow solution of complex former changed and became many times more intense. After a day a lake precipitated. Lakes with nickel (from the sulfate), cobalt (from the nitrate), chromium (from chrome alum), ferric iron (from the chloride), and ferrous iron (from the sulfate) were obtained in this way. All the complexes were orange with a more or less (depending on the cation taken) red tinge, except the last, which was grassy green.

SUMMARY

1. A synthesis of D,L-adrenochrome monooxime and monosemicarbazone, on which there are almost no data in the literature, has been worked out and their properties investigated. The acid dissociation constants of these compounds have been determined from potentiometric titration data.

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*State Institute of Applied Chemistry.

2. The picrates of D,L-adrenochrome monooxime and monosemicarbazone, which are not described in the literature, have been prepared and analyzed.

3. On the basis of a comparison of the color and acid-base properties of adrenochrome and its oxime and semicarbazone, hypotheses on the probable structure of the latter are advanced.

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DERIVATIVES OF BICYCLO(1,2,2)HEPTANE

IV. SOME AMINES AND AMINOALCOHOLS OF THE BICYCLO(1,2,2)-HEPTANE SERIES

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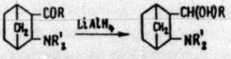
Very recently amines of the bicyclo(1,2,2)heptane series have begun to attract attention because of the high physiological activity of some of them [1, 2]. Not long ago we described the synthesis of aminoketones of this series, namely certain derivatives of 2-acyl-3-dialkylaminobicyclo(1,2,2)heptanes [3]. In connection with the investigation, in progress in our laboratory, of the physiological activity of amines of the bicycloheptane series, we synthesized certain aminoalcohols and amines of this series, which, in the form of the hydrochlorides and alkiodides, were subjected to pharmacological investigation. It was of interest to follow the changes in physiological activity and, in particular, hypotensive action for compounds with the same bicyclo(1,2,2)heptane carbon skeleton and an amino group in position 3, resulting from replacement of the acyl radical in position 2 by a hydroxyalkyl or alkyl group.

As was described in one of the preceding papers [3], the derivatives of 2-acyl-3-aminobicyclo(1,2,2)-heptanes, which were used as starting materials in our work, are very smoothly obtained on treatment of readily accessible 2-acyl-3-chlorobicyclo(1,2,2)heptanes with secondary amines. At present we have synthesized, and in this article describe, three new members of this series: 2-caproyl-3-diethylamino-, 2-acetyl-3-dimethylamino-, and 2-acetyl-3-N-piperidylbicyclo(1,2,2)heptanes. The first of them was prepared according to the general directions [3], whereas the second was prepared in an autoclave, it being necessary to use pure dimethylamine, without difficulty. The preparation of the piperidine analog proved to be the simplest, since piperidine reacts very smoothly with 2-acetyl-3-chlorobicyclo(1,2,2)heptane even at room temperature, and the mixture was heated only to complete the reaction.

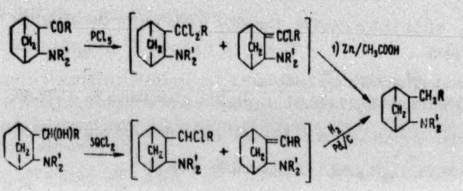
We converted the aminoketones of the bicycloheptane series to the corresponding aminoalcohols by reduction with lithium aluminum hydride.



(I) $R=CH_3$, $R'=C_2H_5$;
(II) $R=CH_3$, $(R')_2=(CH_2)_5$;
(III) $R=C_5H_{11}$, $R'=C_2H_5$.

The process goes very smoothly, and the corresponding aminoalcohols (I), (II) and (III), previously unknown, were obtained in nearly quantitative yields. They were viscous, noncrystallizing oils with a slight odor, which slowly darkened on keeping. Crystalline methiodides were prepared from them with no particular difficulty. The aminoalcohol hydrochlorides are extremely hygroscopic and are purified with difficulty; for pharmacological tests, therefore, solutions of them were prepared by exact neutralization of a portion of the aminoalcohol with dilute hydrochloric acid.

To obtain bicyclo(1,2,2)heptane derivatives of similar structure which do not contain oxygen functions, we tried two routes: from the corresponding aminoketones and from the aminoalcohols.



(IV) $R = CH_3$, $R' = C_2H_5$; (V) $R = CH_3$, $(R')_2 = (CH_2)_5$; (VI) $R = C_5H_{11}$, $R' = C_2H_5$.

In the first route the aminoketone was treated with phosphorus pentachloride in chloroform solution, and the aminochloride hydrochloride thereby obtained as an oil was reduced, without purification, with zinc dust in acetic acid. However, the amine prepared by this method always contained a small percentage of chlorine and gave positive reactions for a double bond, evidently owing to admixture of an unsaturated chloride stable to reduction. By further hydrogenation of this slightly impure amine over palladium black, the pure amine was successfully prepared. We prepared 2-ethyl-3-diethylaminobicyclo(1,2,2)heptane (IV) from 2-acetyl-3-diethylaminobicyclo(1,2,2)heptane by this route with a yield about 40%.

Another route to amines of this type consists in the treatment of aminoalcohols with thionyl chloride; the substances so prepared contained about 3% chlorine and gave a pronounced reaction for the double bond. Thus the main reaction product resulting from the treatment of aminoalcohols with thionyl chloride obviously consisted of unsaturated amines containing admixtures of aminochlorides. We did not attempt to isolate individual substances from the mixtures obtained, but hydrogenated them directly in acetic acid over palladium on carbon. As a result pure amines were obtained with a yield about 40%. 2-Ethyl-3-N-piperidyl- and 2-hexyl-3-diethylaminobicyclo(1,2,2)heptanes (V) and (VI) were synthesized by this route. The amines obtained were oils with the typical, disagreeable odor of higher amines, which slowly darkened on keeping. We successfully prepared crystalline methiodides from amines (IV) and (V); amine (VI) gave an oily methiodide. The hydrochlorides of amines (IV), (V) and (VI) were prepared for pharmacological tests, similarly to those of aminoalcohols (I), (II) and (III).

The pharmacological investigation of the obtained aminoalcohols and amines of the bicyclo(1,2,2)heptane series, and also the corresponding aminoketones described in this and preceding articles [3], was conducted in the pharmacological division of the Iu. V. Uranov Institute of Pharmacology and Chemotherapy (in experiments with cats).

The tests showed that the hydrochlorides of amines, aminoalcohols, and aminoketones are devoid of ganglion-blocking action. On the contrary, aminoketone alkiodides (see [3]) have appreciable ganglion-blocking activity, while aminoalcohol and amine alkiodides manifest such activity only in particular cases, namely those cases where there is a radical containing only two carbon atoms in position 2 of the bicycloheptane ring. The lack of activity of piperidine derivatives is noteworthy.

As regards hypotensive activity, all the derivatives of aminoketones quite definitely lower the blood pressure by amounts which are sometimes considerable. Aminoalcohol alkiodides and hydrochlorides manifest only a feeble hypotensive effect. Most of the compounds which are active with respect to lowering the blood pressure have rather high toxicity.

EXPERIMENTAL

I. 2-Caproyl-3-chlorobicyclo(1,2,2)heptane was prepared by hydrogenation of 2-caproyl-3-chlorobicyclo-(1,2,2)heptane-5 over $Pd/BaSO_4$ in acetone solution, as described earlier, [4], with a yield of 83.5%.

B.p. 132-134° (4 mm), d_4^{20} 1.0458, n_D^{20} 1.4823.
Found %: Cl 15.11, 15.20. $C_{13}H_{21}OCl$. Calculated %: Cl 15.43.

II. 2-Acetyl-3-dimethylaminobicyclo(1,2,2)heptane. A 15.0 g quantity of 2-acetyl-3-chlorobicyclo(1,2,2)-heptane was mixed at −30° with 50 ml of dimethylamine, and the resulting mixture was heated in a metal ampule at 100° for 10 hours. Then the excess dimethylamine was evaporated and collected in a cooled trap, the residue was dissolved in 10% hydrochloric acid, the neutral substances were extracted with ether, the hydrochloric acid solution was made alkaline, the separated aminoketone was extracted with ether, and the extracts were dried with potash and distilled. Yield 12.5 g (79.5%). Colorless liquid with a characteristic amine odor, which gradually darkens on keeping.

B.p. 106-108° (5 mm), d_4^{20} 0.9985, n_D^{20} 1.4850.
Found %: C 73.17, 73.13; H 10.17, 10.06. $C_{11}H_{19}ON$. Calculated %: C 72.88; H 10.56.

Methiodide colorless crystals with m.p. 164-166° (dec.) after reprecipitation from acetone by ether.

Found %: I 38.89, 38.91. $C_{12}H_{22}ONI$. Calculated %: I 39.27.

Ethiodide, m.p. 158-160° (reprecipitated from acetone by ether).

Found %: I 37.61; 37.58. $C_{13}H_{24}ONI$. Calculated %: I 37.68.

III. 2-Acetyl-3-N-piperidylbicyclo(1,2,2)heptane. A 17.0 g quantity of 2-acetyl-3-chlorobicyclo(1,2,2)-heptane was mixed with 50 ml of piperidine. After 5-10 minutes strong, spontaneous heating of the mixture and copious precipitation of piperidine hydrochloride were observed. When spontaneous heating ceased, the reaction mass was heated in a boiling water bath for 3 hours, the excess pyridine was distilled off in vacuo, the residue was poured into water, and the aminoketone was isolated as described above. Yield 17.1 g (77%). Colorless, viscous oil with a characteristic, disagreeable odor; darkened on prolonged standing.

B.p. 120-122° (5 mm), d_4^{20} 1.0278, n_D^{20} 1.5052.
Found %: C 75.96, 75.68; H 10.22, $C_{14}H_{23}ON$. Calculated %: C 75.97; H 10.47.

Methiodide, m.p. 152-153° (purified through reprecipitation from acetone by ether).

IV. 2-Caproyl-3-diethylaminobicyclo(1,2,2)heptane was prepared by heating 22.9 g of 2-caproyl-3-chlorobicyclo(1,2,2)heptane and 75 ml of diethylamine for 10-15 hours according to the general method described earlier by us [3]. Yield 19.5 g (74%). Colorless oil with a characteristic, disagreeable odor, which turned yellow on keeping.

B.p. 127-129° (4 mm), d_4^{20} 0.9461, n_D^{20} 1.4775.
Found %: N 5.39, 5.63. $C_{17}H_{31}ON$. Calculated %: N 5.31.

Methiodide, m.p. 117-118° (purified through reprecipitation from acetone by ether).

Found %: I 31.46, 31.31. $C_{18}H_{34}ONI$. Calculated %: I 31.16.

V. 2-(1-Hydroxyethyl)-3-diethylaminobicyclo(1,2,2)heptane. To a solution of lithium aluminum hydride prepared from 2.8 g of lithium hydride and 20 g of aluminum bromide in 100 ml of absolute ether, 31.0 g of 2-acetyl-3-diethylaminobicyclo(1,2,2)heptane was added, dropwise and with stirring, at such a rate that the reaction mixture boiled gently. The mixture was left for a day at room temperature, the excess lithium aluminum hydride was decomposed with alcohol, 300 ml of 40% sodium hydroxide was added, the ether layer was drawn off, the water layer was twice subjected to ether extraction, and the extracts were added to the main portion of the substance and dried with potash. The aminoalcohol was isolated by distillation. Yield 30.2 g (96%). A colorless, viscous liquid with a weak amine odor; it was kept for a long time without change.

B.p. 115-117° (3 mm), d_4^{20} 0.9694, n_D^{20} 1.4860.
Found %: C 73.58, 73.57; H 11.95, 11.64. $C_{13}H_{25}ON$. Calculated %: C 73.87; H 11.93.

The methiodide was prepared in the usual way and purified through reprecipitation from anhydrous acetone by ether; m.p. 149-150°.

Found %: I 35.90; 35.80. $C_{14}H_{28}ONI$. Calculated %: I 35.92.

VI. 2-(1-Hydroxyethyl)-3-N-piperidylbicyclo(1,2,2)heptane. A 31.0 g quantity of 2-acetyl-3-N-piperidylbicyclo(1,2,2)heptane was reduced with lithium aluminum hydride (from 2.22 g of lithium hydride and 18.6 g of aluminum bromide) in 100 ml of absolute ether, as described in the preceding experiment. Yield of aminoalcohol, 29.2 g (93.5%). Colorless, very viscous oil with a weak amine odor; it gradually turned yellow on prolonged standing.

B.p. 139-141° (4 mm), n_D^{20} 1.5044.
Found %: C 75.30, 75.43; H 11.30, 11.23. $C_{14}H_{25}ON$. Calculated %: C 75.28; H 11.28.

Methiodide, m.p. 140-142° (from anhydrous acetone).

Found %: I 34.88, 34.90. $C_{15}H_{18}ONI$. Calculated %: I 34.74.

VII. 2-(1-Hydroxyhexyl)-3-diethylaminobicyclo(1,2,2)heptane was similarly prepared from 26.5 g of 2-caproyl-3-diethylaminobicyclo(1,2,2)heptane by reduction with lithium aluminum hydride (from 1.6 g of lithium hydride and 13.4 g of aluminum bromide) in 60 ml of absolute ether. Yield 24.8 g (93%). Colorless oil which was kept for a long time without change.

B.p. 146-148° (3 mm), d_4^{20} 0.9382, n_D^{20} 1.4800.
Found %: C 76.59, 76.37; H 12.86, 12.90. $C_{17}H_{33}ON$. Calculated %: C 76.30; H 12.44.

The methiodide separated out in the form of an oil which crystallized on trituration with light petroleum ether. Colorless needles with m.p. 152.5-154° after reprecipitation from acetone by ether.

Found %: I 30.85, 30.79. $C_{18}H_{36}ONI$. Calculated %: I 31.00.

VIII. 2-Ethyl-3-diethylaminobicyclo(1,2,2)heptane. To a suspension of 24.0 g of phosphorus pentachloride in 150 ml of dry chloroform was added 19.0 g of 2-acetyl-3-diethylaminobicyclo(1,2,2)heptane hydrochloride [3]. On stirring, the phosphorus pentachloride dissolved with slight heating, and the reaction mass turned orange. The mixture was stirred for 2 hours at room temperature, after which the solvent was distilled off in vacuo, the residue was shaken three times with absolute ether, and the ethereal solution was decanted from the oily hydrochloride. The 2-(1,1-dichloroethyl)-3-diethylaminobicyclo(1,2,2)heptane hydrochloride so obtained was dissolved in 150 ml of glacial acetic acid, and 40.0 g of zinc dust was added with stirring. When spontaneous heating ceased (about 0.5 hour), the mixture was heated with stirring in a boiling-water bath for 4 hours. Then the precipitate was filtered out, the mother liquor was poured into 400 ml of water, and the aqueous solution was shaken once with ether, in order to extract neutral substances, and made alkaline with solid sodium hydroxide. The amine which separated out was extracted with ether, and the extracts were dried with solid sodium hydroxide and distilled, the fraction with b.p. 107-112° (8 mm), n_D^{20} 1.4816 being collected; weight 12.4 g. The substance had a characteristic amine odor and decolorized a solution of bromine in carbon tetrachloride. It contained about 2% chlorine.

A 12.4 g quantity of the amine obtained was hydrogenated, without further purification, in 30 ml of glacial acetic acid over 1.0 g of palladium black. During 15 hours 1400 ml (0.063 mole) of hydrogen (0°, 760 mm) was absorbed, after which the hydrogenation was stopped. The catalyst was filtered out, the acetic acid solution was diluted with water, neutral substances were extracted with ether, the water layer was made alkaline, the separated amine was extracted with ether, and the extracts were dried with solid caustic and distilled. There was obtained 9.2 g (41%, calculated on the basis of the original aminoketone hydrochloride) of the amine. Colorless liquid with the characteristic odor of amines of the bicyclo(1,2,2)heptane series.

B.p. 73.5-74.5° (1 mm), d_4^{20} 0.9226, n_D^{20} 1.4770.
Found %: C 80.21, 80.09; H 12.65, 12.55. $C_{13}H_{25}N$. Calculated %: C 79.92; H 12.90.

The methiodide was purified through reprecipitation from acetone by ether; colorless leaflets with m.p. 176-176.5°.

Found %: I 37.73, 37.98. $C_{14}H_{28}NI$. Calculated %: I 37.63.

IX. 2-Ethyl-3-N-piperidylbicyclo(1,2,2)heptane. To a solution of 6.3 ml of thionyl chloride in 30 ml of dry chloroform, 9.9 g of 2-(1-hydroxyethyl)-3-N-piperidylbicyclo(1,2,2)heptane was added dropwise during 15 minutes with stirring. The temperature of the reaction mass rose to 40-50°, and the latter turned brown. When the spontaneous heating ceased (1 hour), the mixture was boiled for 2 hours until the evolution of hydrogen chloride and sulfur dioxide had entirely stopped, the solvent and excess thionyl chloride were distilled off in vacuo, the residue was poured into water, and neutral substances were removed from the acidic, aqueous solution by extraction with ether. Then the aqueous solution was made alkaline, the separated amine was extracted with ether, and the extracts were dried with solid caustic and distilled. There was obtained 6.8 g of a mobile liquid with b.p. 118-120° (2 mm) and n_D^{20} 1.5060. The substance decolorized a solution of bromine in carbon tetrachloride and contained about 3% chlorine, being, therefore, a dehydration product of the aminoalcohol with an admixture of the aminochloride.

A 6.8 g quantity of the amine obtained, containing an admixture of the aminochloride, was hydrogenated in 20 ml of glacial acetic acid over 3.5 g of 10% palladium on carbon. During 12 hours 700 ml (0.0314 mole) of hydrogen (0°, 760 mm) was absorbed, after which the hydrogenation was stopped. 2-Ethyl-3-N-piperidylbicyclo(1,2,2)heptane was isolated similarly to 2-ethyl-3-diethylaminobicyclo(1,2,2)heptane. There was obtained 3.2 g of the amine (37%, calculated on the basis of the original aminoalcohol). Colorless, mobile liquid with a characteristic amine odor. It was kept for a long time without change.

B.p. 115-117° (4 mm), d_4^{20} 0.9805, n_D^{20} 1.5040.
Found %: C 80.89, 81.17; H 12.28, 12.34. $C_{14}H_{25}N$. Calculated %: C 81.09; H 12.15.

Methiodide, m.p. 142-143° (reprecipitated from acetone by ether).

Found %: I 36.40, 36.57. $C_{15}H_{28}NI$. Calculated %: I 36.33.

X. 2-Hexyl-3-diethylaminobicyclo(1,2,2)heptane was prepared in a similar manner. From 13.0 g of 2-(1-hydroxyhexyl)-3-diethylaminobicyclo(1,2,2)heptane, after treatment with 10 ml of thionyl chloride in 70 ml of dry chloroform, there was obtained 10.2 g of a substance with b.p. 123-125° (1 mm), d_4^{20} 0.9131, n_D^{20} 1.4830, which decolorized a solution of bromine in carbon tetrachloride and contained about 3% chlorine.

On hydrogenation of the unsaturated amine, containing an admixture of the aminochloride, in 30 ml of glacial acetic acid over 4.0 g of 10% palladium on carbon, 930 ml (0.0415 mole) of hydrogen (0°, 760 mm) was absorbed during 10 hours. Yield 7.8 g (39.8%, calculated on the basis of the original aminoalcohol). Colorless liquid with a characteristic amine odor. It was kept for a long time without change.

B.p. 112-113° (1 mm), d_4^{20} 0.9032, n_D^{20} 1.4800.
Found %: C 81.20, 81.25; H 12.89, 13.02. $C_{17}H_{33}N$. Calculated %: C 81.20; H 13.22.

Hydrochloride and methiodide – oils which did not crystallize and could not be purified.

SUMMARY

1. 2-(1-Hydroxyalkyl)-3-dialkylaminobicyclo(1,2,2)heptanes have been prepared by the reduction of 2-acyl-3-dialkylaminobicyclo(1,2,2)heptanes with lithium aluminum hydride.

2. 2-Alkyl-3-dialkylaminobicyclo(1,2,2)heptanes have been prepared by two routes: a) treatment of 2-acyl-3-dialkylaminobicyclo(1,2,2)heptanes with phosphorus pentachloride, followed by reduction with zinc dust and hydrogenation, and b) treatment of 2-(1-hydroxyalkyl)-3-dialkylaminobicyclo(1,2,2)heptanes with thionyl chloride, followed by hydrogenation.

3. The question of the dependence of physiological action on structure in a series of amino derivatives of bicyclo(1,2,2)heptanes has been discussed.

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-Index-

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AUTHOR INDEX

1958

Abdurasuleva. A. R. Cycloalkylation of Phenols and Their Ethers. I. Condensation of Phenol with Cyclohexanol-3022
Abidova, M. F., see Sultanov, A. S.-765
Abramov, V. S., L. Sh. Belokon' and F.I . Makhmutova. Reaction of Dialkyl Phosphorous Acids with Aldehydes and Ketones. Esters of 1-Hydroxy-1-Acetoethylphosphonic and 2-Hydroxy-4-Keto-2-Amylphosphonic Acids-647
Abramov, V. S., and M. I. Kashirskii. On the Reaction of Aryl(Alkyl)Phosphinic Acids with Aldehydes and Ketones. XIX. Esters of α-Hydroxyalkylphenylphosphinic Acids-3090
Abramov, V. S., and N. A. Semenova. On the Reaction of Dialkyl Hydrogen Phosphites with Aldehydes and Ketones. XVIII. Phenyl Esters of α-Hydroxyalkylphosphonic Acids-3087
Abramova, E. A. Comparative Distribution of Carbon Disulfide in the Main and Side Reactions in the Preparation of Viscose at Low Temperature and Under Normal Conditions-3245
Abramova, E. I., see Khmelevskii, V. I.-2012
Abramova, E. I., see Khmelevskii, V. I.-2016
Abrazhanova, E. A., see Kretov, A. E.-2802
Abubakirov, N. K., V. A. Maslennikova and M. B. Gorovits. A Study of Glucosides of Jute. I. Olitoriside-2316
Aizikovich, M.A., I. A. Maretina and A. A. Petrov. Catalytic Hydrogenation of Vinylethylene Oxides. I. Hydrogenation of Butadiene Oxide-3076
Aizikovich, M. A., and A. A. Petrov. Catalytic Hydrogenation of Vinylethylene Oxides. II. Hydrogenation of Chloroprene Oxide- 3082
Akhrem, A. A., see Nazarov, I. N.-1511
Akhrem, A. A., see Nazarov, I. N.-1838
Akhrem, A. A., see Nazarov, I. N.-1850
Akhrem, A. A., see Nazarov, I. N.-2227
Akhrem, A. A., see Nazarov, I. N.-2237
Akhrem, A. A., see M. E. Vol'pin-326
Akimova, L. N., I. P. Kuranova and N. I. Gavrilov. Models of the Microstructures of Protein. III. The Structure of Phenylalanine Anhydride Derivates-391
Akopian, A. N., A. M. Saakian and M. G. Avetian. The Synthesis and Investigation of the Chlorination Products of Acetylenyldivinyl(1,3-Hexadiene-5-Ine)-1276
Aladzheva, I. M., see Pudovik, A. N.-2532
Al'bitskaia, V. M., and A. A. Petrov. Investigation of the Chemistry of Organic Oxides. XIV. Reaction of the α-Oxide of Isoprene with Ammonia and Amines-873
Aleksandrova, G. V., see Nazarov, I. N.-2227
Aleksandrova, G. V., see Nazarov, I. N.-2237
Aleksandrovich, M. K., see Koz'mina, O. P.-3230
Aliev, A. F., see Shamkhal Mamedov-897
Alikhanov, P. P., see Shatenshtein, A. I.-2666
Almashi, L. F, see Lebedeva, A. I.-876
Al'perovich, M. A., I. K. Ushenko and L. N. Tiurina. Synthesis of Thiacarbocyanines with Unsaturated Radicals as Substituents-2573
Ambrush, Ivan., see Kochetkov, N. K.-3053
Ambrush, T. I., see Kochetkov, N. K.-3053
Andreev, D. N., see Korshak, V. V.-2039
Andreev, P. A., see Kreshkov, A. P.-188
Andreeva, E. I., see Bocharnikova, A. V.-2918
Andreeva, M. A., and B. I. Stepanov. Halogen Displacement in Azo Compounds. V. Reaction of the Copper Complex of 2-Chlorobenzeneazo-2'-Naphthol with Alkoxides-2995
Andreeva, M. A., see Stepanov, B. I.-2525
Andreeva, N. V., see Shchukarev, S. A-2040
Andrianov, K. A., S. Dzhenchel'skaia and Iu. Petrashko. Catalytic Polymerization of Polyphenyl- and Poly(Dimethylphenyl)Siloxanes-666
Andrianov, K. A., M. Ia. Levshuk, S. A. Golubtsov and T. A. Krasovskaia. Simultaneous Hydrolysis of Mono- and Trifunctional Alkyl(aryl)chlorosilanes-330
Androsov, A. N., see Litvinenko, L. M.-2086
Anikeeva, A. N., and G. M. Zarubinskii. Allyl and Methallyl Esters of Acetals and Ketals of Xylitol and Xylitan-3233
Anikeeva, A. N., see Temnikova, T. I.-3194
Antonov, V. K., see Braz, G. I.-3001
Ardashev, B. I., and V. I. Minkin. Investigations in the Field of Quinoline Derivatives XVII. Synthesis of some 6- and 8- Alkoxyquinolines-535
Ardashev, B. I., and V. I. Minkin. Investigations in the Field of Quinolines by Rearrangement of Acylated Arylamines-1627
Ardashev, B. I., see Minkin, V. I.-2590
Ariia, S. M., and M. P. Morozova. The Properties of Salt-Form Compounds of Variable Composition and Views on Their Chemical Structure-2647
Artamonov, P. A. Preparation of Oxides of α, β-Unsaturated Higher Fatty Acids and Study of Their Properties-1414

Artsybasheva, Iu. P., and I. A. Favorskaia. Homologs of Monovinylacetylene. VIII. Spectral Characteristics of an Enyne Hydrocarbon,3',3'-Metho-3-Ethylbuten-3-Yne-1- and Its Derivatives-3266
Artsybasheva, Iu. P., see Favorskaia, I. A.-1832
Askarov, M. A., see Fedotova, O. Ia. -753
Auvinen, E. M., see Favorskaia, I. A.-1832
Avaeva, S. M., see Botvinik, M. M.-1583
Avericheva, V. E., see Savintsev, P. A.-1748
Avetian, M. G., see Akopian, A. N.-1276
Avramenko, V. G., see Rodionov, V. M.-2279

Babaian, A. T., G. M. Mkrian and R. S. Giuli-Kevkhian. Investigations on Amines and Quaternary Ammonium Compounds. X. Preparation of Isoprene from α,β- and γ,γ-Dimethylallyl chlorides-1314
Babak, S. F., and G. B. Kagramanova. Interaction of Halides of Trivalent Iron with Nicotine-1312
Babak, S. F., see Kondrashov, I. A.-1753
Babichev, F. S., and A. I. Kiprianov. On the Products of Reaction Between Methylene Bases of Benzothiazole and Benzselenazole and Alkyl Halides-209
Babievskii, K. I., see Nikolenko, L. N.-238
Badenkova, L. P., see Nazarov, I. N.-1195
Baev, I. F., see Sigov, O. V.-1337
Bainova, M. S., see Bazilevskaia, G. I.-1065
Bainova, M. S., see Evstigneeva, R. P.-1241
Bakanova, Z. M., see Mel'nikov, N. N.-2507
Balandin, A. A., see Roge, T. V.-2937
Bal'ian, Kh. V., Z. A. Lerman and L. A. Merkur'eva. Hydrogenation in the Presence of Colloidal Palladium. IX. Hydrogenation of Vinylpropyl- and Vinylbutylacetylenes-110
Bal'ian, Kh. V., see Petrov, A. A.-1490
Balonova, E. M., see Kuznetsov, S. G.-618
Bankovskii, Iu. A., A. F. Ievin'sh and E. A. Luksha. A Simplified Synthesis of 8-Mercaptoquinoline (Thiooxine) and Preparation of Its Potassium and Sodium Salts-2310
Bankovskii, Iu. A., and E. F. Lobanova. Synthesis of 6-Bromo-8-Mercaptoquinoline (6-Bromothiooxine) and Some of Its Properties-2884
Baranaev, M. K., Iu. M. Zinov'ev, T. K. Skripach and L. Z. Soborovskii. Synthesis of Organophosphorus Compounds from Hydrocarbons and Their Derivatives. VII. A Study of Oxidation of Phosphorus Trichloride by Oxygen-1678
Baranchik, N. M., I. V. Grachev and D. Z. Zavel'skii. The Structure and Transformations of Methylaryl-N-Nitrotriazenes. III. On Some Properties of Methylaryl-N-Nitrotriazenes-1400
Baranov, S. N., F. A. Zhoglo and R. V. Vizgert. Synthesis of Some Esters of 4,4'-Dihydroxydiphenyl Sulfone and Carboxylic Acids-1330
Baranov, S. N., see Grishchuk, A. P.-869
Bardyshev, I. I., and V. V. Kokhomskaia. Resin Acids. I. The Nature of α-Sapinic Acid-528
Bardyshev, I. I., and L. I. Ukhova. Resin Acids. II. The Nature of β-Sapinic Acid-532
Barkhash, V. A., see Machinskaia, I. V.-2899
Barkhudarian, M. G., see Klebanskii, A. L.-554
Barkhudarian, M. G., see Klebanskii, A. L.-559
Barkhudarian, M. G., see Klebanskii, A. L.-853
Barkhudarian, M. G., see Klebanskii, A. L.-3279
Batuev, M. I., Discussion Series. Conjugation in and the Dual Reactivity of Butadiene-2930
Batuev, M. I. Disscussion Forum. The Problem of Conjugation in Benzene-3177
Bazilevskaia, G. I., D. V. Gura, M. S. Bainova, K. M. Diumaev, I. K. Sarycheva and N. A. Preobrazhenskii. The Synthesis of Tropane-3-α-ol, Tropine-1065
Bazilevskii, M. V., see Kochetkov, N. K.-2762
Bedniagina, N. P., G. A. Panifilov and I. Ia. Postovskii. Chemistry of Naphthacene. VII. Nitration of Naphthacene-361
Beiles, R. G. Interaction of Aqueous Solutions of Salts of Tetravalent Titanium with Pyrazolone Derivatives-1631
Bekhevkin, I. M., and E. G. Veselkova. Physicochemical Analysis of Binary Systems Formed by Phenol with Acetic Acid and Its Chloro Derivatives-795
Bekhli, A. F. Mechanism of the Reaction of Transamination in the β-Dialkylaminopropionitrile Series-204
Bekhli, A. F. Chemical Structure and Parasitocidal Activity. XXI. Concerning the Problem of the Connection of the Structural Stability of Derivatives of 9-Aminoacridine and Their Antimalarial Action-1943
Bekhli, A. F. Chemical Structure and Parasitocidal Activity. XXII. Concerning the Problem of the Connection Between the Structure and the Antimalarial Action of Isomeric Chloro-4-Aminoquinolines-1946
Beliakova, Z. V., see Iur'ev, Iu. K.-1
Beliakova, Z. V., see Iur'ev, Iu. K.-1803
Beliakova, Z. V., see Iur'ev, Iu. K.-2408
Beliakova, Z. V., see Iur'ev, Iu. K.-2789
Belianina, E. T., see Liubomilov, V. I.-322
Belinskaia, R. V., see Iagupol'skii, L. M.-750
Belinson, Z. Ia., see Tsukervanik, I. P.-2077
Belokon', L. Sh., see Abramov, V. S.-647
Belonovich, M. I., see Lapkin, I. I.-586
Belov, V. N., see Kologrivova, N. E.-1325
Belov, V. N., see Kologrivova, N. E.-3136
Belov, V. N., see Svadkovskaia, G. E.-2305
Benderskii, V. A., see Tatevskii, V. M.-1781
Berdichevskii, E. G., F. Iu. Rachinskii and E. K.

Novoselova. Some Derivatives of Mercaptocaffeine and Mercaptotheobromine-670
Berdinskii, I. S. Substituted Hydrazides of Hydroxycarboxylic Acids. II. Synthesis of Arylhydrazides of Dialkylglycolic Acids-1318
Berezina, B. B., see Lutkovza, V. I.-1320
Berezovskii, V. M., and E. P. Rodinova. The Synthesis of 5,6,7-Trimethylisoalloxazines-1016
Berezovskii, V. M., and Iu. P. Sobolev. Electrolytic Reduction of 2,4-Diamino-5-isonitroso-6-hydroxypyrimidine-262
Berezovskii, V. M., see Khomiakov, V. G.-2925
Berga, S. E., see Romadan, I. A.-405
Bergelson, L. D., see Nazarov, I. N.-1195
Berkman, Ia. P., see Vizgert, R. V.-2158
Berlin, A. Ia., and M. N. Vasil'eva. Synthesis of the Diethyleneimide of 4-Methyluracil 5-Methylene Phosphinic Acid-1033
Besuglyi, V. D., V. N. Dmitrieva and V. V. Dorofeev. Polarographic Study of Aminoacetophenones-305
Bezuglyi, V. D., see Dmitrieva, V. N.-2059
Biktimirova, L. G., see Pudovik, A. N.-1545
Bliaeva, I. N., see Iakubovich, A. Ia.-660
Blidin, V. P., and T. G. Golovanova. Polytherm of the Ternary System Urea-Citric Acid-Water-2955
Blizniukov, V. I., and N. T. Solonskaia. The Absorption Spectra and Structure of Substituted Quinolines Serving as Starting Substances of Antimalarials. V. Structure and Tautomerism of the 2- and 4-Aminoquinolines-1293
Blizniukov, V. I., and A. K. Sukhomlinov. The Absorption Spectra and Structure of Acridine-1301
Blizniukov, V. I., and A. K. Sukhomlinov. Absorption Spectra and Structure of the Bisulfite Compound of Acridine-1659
Blizniukov, V. I., and A. K. Sukhomlinov. Absorption Spectra and Structure of 2-Methoxyaminoacridine-9-1662
Blokh, G. A., and V. S. Zdanovich. Isotope Exchange of 2-Mercaptobenzthiazole Sulfur and Elementary Sulfur in the Presence of Amines-2680
Bobinova, L. M., see Razuvaev, G. A.-1672
Bobrova, M. I., and A. N. Matveeva-Kudasheva. Polarographic Determination of Nitriles-2958
Bobrova, M. I., and A. N. Matveeva-Kudasheva. Polarography of the Thermal Decomposition of 2,2'-Azobisisobutyronitrile in Vinyl Butyl Ether and Methyl Methacrylate-3323
Bobysheva, Z. I., see Kuznetsov, S. G.-511
Bobysheva, Z. I., see Kuznetsov, S. G.-618
Bocharnikova, A. V., and E. I. Andreeva. A New Alkaloid from the Central Asiatic Larkspur-2918
Bocharnikova, A. V., see Kuzovkov, A. D.-547
Bogdanov, M. N. Chloromethylation of Saturated α,ω-Phenylaliphatic Acids-1670
Bogdanov, S. V. The Reduction of the Bisulfite Compound of 1-Naphthol. 1. 1,2-Dihydronaphthalene-2-Sulfonic Acid-1382
Bogdanov, S. V. The Reduction of the Bisulfite Compound of 1-Naphthol and Its Oxime-1386
Bogdanova, E. S., see Gorin, Iu. A.-170
Bogdanova, L. I., see Gorin, Iu. A.-640
Bogoslovskii, N. A., see Iakubovich, A. Ia.-316
Bogoslovskii, N. A., see Iakubovich, A. Ia.-2325
Bokhovkin, I. M. Physicochemical Investigation of the Interaction of Acetone with Acetic Acid and Its Derivative-835
Boksiner, E. I., see Dashkevich, L. V.-2872
Boldyrev, B. G., and Iu. I. Kofman. Investigations on Thiosulfonic Acids. III. Alkyl Esters of Phenylmethane Thiosulfonic Acid and Their Antibacterial Properties-746
Boldyrev, B. G., and T. A. Trofimova. A Study in the Field of Thiosulfonic Acids. IV. Concerning the Mechanism of the Reaction of Formation of Thiosulfonates-1981
Borisov, S. N., M. G. Voronkov and B. N. Dolgov. On the Reactions of Alkyldichlorosilanes with Chlorinated Hydrocarbons-3318
Borisova, N. T., see Kostsova, A. G.-2457
Bortrukova, M. M., see Shchukarev, S. A.-3315
Botvinik, M. M., and S. M. Avaeva. The Fermentative Synthesis of N-Peptides from O-Peptides of β-Hydroxyamino Acids-1583
Braude, M. B. Mechanism of the Reduction of γ-Acetobutyronitrile-1368
Braz, G. I., V. K. Antonov and K. N. Kurdiumova. Some Ethylenimino-1,3,5-Triazines-3001
Bruker, A. B., R. I. Frenkel' and L. Z. Soborovskii. Preparation of Esters of Fluoroantimonious and Fluorotitanic Acids by Treatment of the Complete Esters of These Acids with Antimony Trifluoride-2450
Bruker, A. B., and B. B. Levin. Some Considerations on the Mechanism of the Formation of Mercury Aromatic Compounds by the Oxidation of Arylhydrazines with Mercuric Salts-2752
Bruker, A. B., and N. M. Nikiforova. A New Method for the Preparation of Organoarsenic Compounds by the Oxidation of a Mixture of Phenylhydrazine and Arsenic Trichloride with Atmospheric Oxygen in the Presence of Cupric Chloride-2445
Bruker, A. B., T. G. Spiridonova and L. Z. Soborovskii. Reaction of Tetrafluoroethylene with Arsenic Trichloride in the Presence of Aluminum Chloride-347
Bruker, A. B., see Zeide, O. A.-2442
Budovskii, E. I., see Kochetkov, N. K.-3042
Bukreeva, L. M., see Sergeev, P. G.-101
Bulatova, N. V., see Plisov, A. K.-489

Burmakin, N. M., see Kogan, L. M.-27
Bursian, N. R., see Maslianskii, G. N.-2684
Bursian, N. R., see Maslianskii, G. N.-2690
Butsko, S. S., and B. Ia. Dain. The Spectrophotometric Investigation of the Reaction of Chlorophyll with Ferric Chloride-2636
Buzanov, M. I., see Gavrilov, B. G.-2750
Bykov, G. V. Electron Charge Density of Chemical Bonds and the Chemical Properties of Molecules. I. Energies of Activation of Substitution Reactions at a Saturated Carbon Atom-568

Ch'ang Ch'ung Kwang, see Nazarov, I. N.-127
Chebotareba, E. G., see Pudovik, A. N.-2527
Chel'tsova, M. A., A. D. Petrov and Iu. P. Egorov. Organomagnesium Synthesis and Properties of 1,1,1-Triphenylalkylmethanes, 1,5-Diphenyl-3-Benzylpentane, and 1-Phenyl-3-(2-Phenylethyl)-Tridecane. II-920
Chen Chang-Pai, R. P. Evstigneeva and N. A. Preobrazhenskii. Synthesis of 2-(α-Pyridyl)-3-(β-Hydroxyethyl)-Indole-3116
Ch'en Shu-feng, see Ch'ih Yueh-fon -1533
Cherenkova, L. I., see Petrov, A. V.-1490
Cherkasov, V. M., see Nirenburg, V. L.-198
Cherkasova, E. M., see Nazarov, I. N.-122
Cherkasova, E. M., see Nazarov, I. N.-127
Cherkasova, V. A., see Domnin, N. A.-1520
Cherkasova, V. A., see Domnin, N. A.-2103
Cherkasova, V. A., see Domnin, N. A.-2371
Chernetskii, V. N., see Gladshtein, B. M.-2145
Chernetskii, V. N., see Soborovskii, L. Z.-1909
Chernetskii, V. N., see Soborovskii, L. Z.-1913
Cherniak, N. V., see Kogan, L. M.-27
Chernova, I. I., see Gorbacheva, I. N.-167
Chernyshev, E. A., M. E. Dolgaia, Iu. P. Egorov, L. V. Semenov and A. D. Petrov. Silicoalkylation of Aromatic Compounds by Dichloroalkylsilane Chlorides-593
Chernyshev, E. A., M. E. Dolgaia and Iu. P. Egorov. Interaction of γ-Chloropropylsilane Chlorides with Aromatic Compounds by Friedel-Crafts Reaction-2853
Ch'ih Yueh-fon and Ch'en Shu-feng. Investigations in the Pyrimidine Series. Action of Hydrogen Peroxide on Mercaptopyrimidines. Formation of Pyrimidine Sulfones and Their Instability in the Presence of Hydrogen Peroxide-1533
Ch'ih Yueh-fon and Zin Shin-yung. Investigations in the Thiazole Series. V. Synthesis of 2-δ-Amino-n-butyl-4-N-diethylaminomethylthiazole-1542
Chiurdoglu, G., Ch. Goldenberg and J. Geeraerts. Letter to the Editor-1086
Chizhov, A. K., and M. V. Rubtsov. The Synthesis of 1-Azabicyclo-[3,2,1]-Octane-7-Carboxylic Acid-1238
Chizhov, A. K., see Sergievskaia, S. I.-1884
Chizhov, A. K., see Sergievskaia, S. I.-1890
Chizhov, O. S., see Khorlin, A. Ia.-3370
Chlenova, R. S., Ts. M. Gel'fer and S. F. Petrov. Some Derivatives of Phenoxazone - 3006
Chou Ch'in, see Pesin, V. G.-2126
Chou Ch'in, see Pesin, V. G.-2131
Chou Ch'ing, see Khaletskii, A. M.-2845
Chou Ts'in, see Khaletskii, A. M.-2386
Chuchukina, L. G., see Verezin, I. V.-2746
Chugreeva, N. V. Research in the Field of Substituted Phenylosazones and Phenylhydrazones. II. Some New Nitrophenylosazones of Dihydroxytartaric Acid-1424
Chugunov, V. S. Synthesis and Properties of Tetrakis-(tribenzylsiloxy)-silane and Tetrakis(tribenzylsiloxy)methane-333
Chukhina, E. I. The Synthesis of o-Carboxy- and o-Carboxydimethoxybenzalbarbituric Acids-2615

Dain, B. Ia., see Butsko, S. S.-2636
Danilov, S. N., N. F. Gintse and K. V. Levitskaia. Chemistry of Xanthates and Viscose. VIII. Investigation of Polythio Compounds and the Composition of Viscose, Using Labelled Atoms-2978
Danilov, S. N., N. F. Gintse and M. G. Okun'. The Chemistry of Xanthates and Viscose. IX. The Detection of Polysulfide Compounds in Viscose and Their Role-3221
Danilov, S. N., and A. A. Lopatenok. Anhydro, Desoxy and Unsaturated Derivatives of Polysaccharides. I. Desoxycellulose from Cyanoethoxycellulose-3213.
Danilov, S. N., and A. A. Lopatenok. Anhydro, Desoxy and Unsaturated Derivatives of Polysaccharides. II. The Synthesis of Anhydrocellulose from p-Toluenesulfonic Esters-3218
Danilov, S. N., and E. A. Plisko. The Study of Chitin. III. Hydroxyethyl and Ethyl Ethers of Chitin-2255
Danilova, V. N., see Gorenbein, E. Ia.-1445
Dashkevich, L. B., and E. I. Boksiner. Organomagnesium Synthesis with Carbon Suboxide. I-2872
Dashkevich, L. B., and V. S. Karpinskii. Synthesis of Acetylcholine Labelled with Radioactive Carbon C^{14} in the Ester Group-3040
Daukshas, V. K., see Levina, R. Ia.-2089
Davidenko, N. K. The Dissociation Constants of Trihydroxyglutaric Acid-832
Davydova, S. L., see Stepanov, F. N.-864
Davydova, V. P., and M. G. Voronkov. Studies in the Field of Alkoxysilanes. XI. Reaction of Dialkyldiacetoxysilanes with Glycerol and Pentaerythritol-1922

Davydova, V. P., see Voronkov, M. G.-2167
Dediukhina, L. A., see Stepanov, B. I.-1956
Dediukhina, L. A., see Stepanov, B. I.-1962
Delimarskii, Iu. K. The Causes of the Transposition of Metals in the Electromotive Force Series in Fused Electrolytes-1079
Denisova, S. I., M. F. Petrova and G. P. Men'shikov. The Splitting of Macrotominic Acid and Acids from Heliosupine in Caustic Alkali Solutions-1925
Derevitskaia, V., M. Prokof'eva and Z. Rogovin. A Study of the Comparative Reactivity of the Hydroxyl Groups in Cellulose. V. The Distribution of Methoxy Groups in Partly Methylated Cellulose Obtained in an Alkaline Medium at Different Concentrations of Alkali-697
Derevitskaia, V., M. Prokof'eva and Z. Rogovin. A Study of the Comparative Reactivity of the Hydroxyl Groups in Cellulose. VI. The Distribution of Methoxy Groups in the Products of the Methylation of Na Cellulose Alcoholate-700
Derevitskaia, V., M. Prokof'eva and Z. Rogovin. Investigation of the Relative Reactivity of the Hydroxyl Groups of Cellulose. VII. On the Distribution of Methoxyl Groups in Partially Methylated Cellulose, Obtained from Cellulose Treated with Sodium Isoamylate-1427
Derkach, G. I., see Kirsanov, A. V.-1283
Derkach, G. I., see Kirsanov, A. V.-1930
Derkach, G. I., see Kirsanov, A. V.-2283
Derkach, G. I., see Shevchenko, V. I.-1054
Dianov, M. P., and N. A. Trifonov. Physicochemical Analysis of the System Ethylenediamine-Allyl Mustard Oil-845
Diatlovitskaia, S. V., see Iur'ev, Iu. K.-2413
Dionis'ev, D. E., see Tsvetkova, N. K.-840
Dionis'ev, D. E., see Tsvetkova, N. K.-1750
Diumaev, K. M., see Bazilevskaia, G. I.-1065
Diurnbaum, V. I., see Domnin, N. A.-1520
Dmitrevskaia, O. I. Ternary Reciprocal System of Sodium and Potassium Formates and Nitrates-295
Dmitrevskaia, O. I. Ternary Reciprocal System of the Butyrates and Nitrates of Sodium and Potassium-2046
Dmitrevskaia, O. I., and N. M. Sokolov. The Ternary Mutual System of the Propionates and Nitrates of Sodium and Potassium-2949
Dmitrieva, V. N., and V. D. Bezuglyi. Polarographic Investigation of p-Nitrosodimethylaniline-2059
Dmitrieva, V. N., see Besuglyi, V. D.-305
Dobromil'skaia, I. M., see Dolgopol'skii, I. M.-1829
Dokunikhin, N. S., and L. A. Gaeva. Derivatives of Benz-(c,d)-Indoline. I. Thionaphthostyryl and N-Methylthionaphthostyryl-2698
Dokunikhin, N. S., and L. A. Gaeva. Benz[c,d]Indoline Derivatives. II. 6-Benzoylbenz[c,d]Indoline-2-One and the Products of Their Cyclization-2974
Dokunikhin, N. S., and T. N. Kurdiumova. A Study in the Field of Polycyclic Quinones. III. Reaction of 1-Haloanthraquinone with Secondary Alkaromatic Amines-2021
Dokunikhin, N. S., and I. D. Pletneva. Reaction of Hydrazine with Nitro Compounds of the Anthraquinone Series. II. Synthesis of Vat Dyes-Derivatives of Pyrazoleanthronecarboxylic Acid-991
Dolgaia, M. E., see Chernyshev, E. A.-593
Dolgaia, M. E., see Chernyshev, E. A.-2853
Dolgoplosk, B. A., see Tiniakova, E. I.-1682
Dolgoplosk, B. A., see Tiniakova, E. I.-3295
Dolgopol'skii, I. M., A. V. Tumanova, I. M. Dobromil'skaia and M. F. Egudina. Synthesis of 2-Ethyl- and 2-Propyl-1,3-Butadienes-1829
Dolgov, B. N., N. P. Kharitonov, N. E. Glushkova and Iu. I. Khudobin. Catalytic Dehydrocondensation of Trialkylsilanes with Alcohols in the Presence of Metal Chlorides-2737
Dolgov, B. N., N. P. Kharitonov and T. V. Tsukshverdt. Catalytic Dehydrocondensation of Trialkylsilanes with Glycols-2741
Dolgov, B. N., V. V. Mazurek and V. A. Krol'. Effect of Dilution on the Activity of Copper Catalyst in the Dehydrogenation of Butyl Alcohol-2433
Dolgov, B. N., see Borisov, S. N.-3318
Dolgov, B. N., see Golodnikov, G. V.-2134
Dombrovskii, A. V., see Irkevich, A. M.-226
Domnin, N. A., and Stepan Nikolaevich Danilov. (For his seventieth birthday and the forty-fifth anniversary of his scientific and teaching activity)-3190
Domnin, N. A., and V. A. Cherkasov. Studies in the Field of Polymethylene Rings. XXXI. The Reaction of 1-Chloro-1,2-dibromocyclohexane with Quinoline-2103
Domnin, N. A., and V. A. Cherkasova. Investigations on Polymethylene Rings. XXXXII. Transformations of Cyclohexene in Conjugated Halogenations and Dehalogenations-2371
Domnin, N. A., Diurnbaum, V. I., and V. A. Cherkasova. Investigations in the Field of Polymethylene Rings. XXX. Reaction of Diacetyl and Dibenzoyl with Dimethylhydrazine-1520
Dorofeev, V. V., see Besuglyi, V. D.-305
Dubrova, E. V., see Shostakovskii, M. F.-3337
Dubrovina-Samoilova, O. D. Cyclic Esters of Antimonous Acid-2962
Dubykina, N. V., see Kochetkov, N. K.-2437
Dudinskaia, A. A., see Rodionov, V. M.-2279
Dudinskaia, A. A., see Suvorov, N. N.-1430

Dudinskaia, A. A., see Suvorov, N. N.-1433
Dudinskaia, A. A., see Suvorov, N. N.-2634
Dzagnidze, K. Ia., see Nogaideli, A. I.-116
Dzhenchel'skaia, S., see Andrianov, K.-666

Efimova, L. F., see Kabachnik, M. I.-1618
Efremova, V. N., see Plotkina, S. A.-1322
Efros, A. M. Cyanoethylation of Benzimidazolone and Mercaptobenzimidazole-599
Efros, L. S., and A. V. El'tsov. Investigations on Imidazole Derivatives. XVIII. The Problem of the Nitration of 5-Methylbenzimidazole-64
Efros, L. S., and A. V. El'tsov. Investigations on Imidazole Derivatives. XIX. Amino Derivatives of Benzimidazolone and 1,3-Dimethylbenzimidazolone-433
Efros, L. S., and A. V. El'tsov. Imidazole Derivatives. XX. Some Amino Derivatives of Benzimidazolone-916
Efros, L. S., and A. V. El'tsov. Some Amino Derivatives of Piazselenole-2211
Efros, L. S., and A. V. El'tsov. Investigation in the Field of Imidazole Derivatives. XXI. Synthesis and Properties of Imidazolobenzenes-2214
Efros, A. M., see Zakharova, A. I.-3270
Egorov, Iu. P., E. P. Kaplan, Z. I. Letina, V. A. Shliapochnikov and A. D. Petrov. On the Order of Addition of Lithium to Biphenyl-3284
Egorov, Iu. P., see Chel'tsova, M. A.-920
Egorov, Iu. P., see Chernyshev, E. A.-593
Egorov, Iu. P., see Chernyshev, E. A.-2853
Egorov, Iu. P., see Meshcheriakov, A. P.-2621
Egorov, Iu. P., see Novikov, S. S.-2342
Egorov, Iu. P., see Petrov, A. D.-589
Egorova, L. A., see Gur'ianova, E. N.-1794
Egorova, N. L., see Kirsanov, A. V.-1023
Egorova, N. L., see Kirsanov, A. V.-1636
Egudina, M. F., see Dolgopol'skii, I. M.-1829
Eliakov, G. B., see Iur'ev, Iu. K.-1361
Eliakov, G. B., see Iur'ev, Iu. K.-1603
Eliakov, G. B., see Iur'ev, Iu. K.-2789
Elina, A. S. N-Oxides of the Quinoxaline Series. II. N-Oxides of β-(Quinoxalyl-2)-propionic and β-(Quinoxalyl-2)-acrylic Acids-1437.
El'tsov, A. V., see Efros, L. S.-64
El'tsov, A. V., see Efros, L. S.-433
El'tsov, A. V., see Efros, L. S.-916
El'tsov, A. V., see Efros, L. S.-2211
El'tsov, A. V., see Efros, L. S.-2214
Emel'ianov, N. P., and S. F. Naumova. Absorption Spectrum of 1,3-Cyclohexadiene in the 220-300 mμ Region-1342
Emlis, V. S., see Razuvaev, G. A.-1672
Englin, A. L., see Motsarev, G. V.-1395
Enisherlova, O. M., see Maimind, V. I.-2260
Ermolaev, K. M., see Maimind, V. I.-2260
Ermolenko, I. N., and M. M. Pavliuchenko. The Kinetics of Oxidation of Cellulose by Nitrogen Peroxide According to Data Obtained from the Absorption Spectra of the Products-704
Erykalov, Iu. G., see Spryskov, A. A.-1688
Esafov, V. I. An Investigation of the Thermal Decomposition of Etherates of Magnesium Iodide. I. On the Chemism of Oxonium Compounds-1267
Esafov, V. I. An Investigation of the Thermal Decomposition of the Reaction Products of Dioxan with Magnesium Iodide Dietherate, Magnesium Iodide and a Mixture of Magnesium and Iodine-1273
Etlis, V. S., and Razuvaev, G. A. The Preparation and Properties of Some Aryl Derivatives of Thioxanthenol-5-Dioxide with Indicator Properties-1280
Etlis, V. S., see Spasskaia, I. F.-1872
Etlis, V. S., see Spasskaia, I. F.-3033
Evdakov, V. P., see Kucherov, N. F.-2005
Evreinova, E. B., see Kost, A. N.-503
Evstigneeva, R. P. Studies in the Series of Isoquinoline Compounds. XIV. Esters of Isomeric 4',5'-Dimethoxy-6-ethyl-3,4,5,6,7,8-hexahydrobenzo-(1,2:1',2')-quinolizyl-7-Acetic Acids-2494
Evstigneeva, R. P., R. G. Glushkov and N. A. Preobrazhenskii. Studies in the Series of Isoquinoline Compounds. XV. Synthesis of Isomeric o-Methylpsychotrines-2499
Evstigneeva, R. P., N. M. Kashnikova, M. S. Bainova and N. A. Preobrazhenskii. Investigation in the Isoquinoline Series. XII. Synthesis of 4',5'-Dimethoxy-5,6-Dimethyl-7-(1"-Methyl-6",-7"-Dimethoxy-1",2",3",4"-Tetrahydroisoquinolyl)-3,4,5,6,7,8-Hexahydrobenzo[1',2':
:1,2]Quinolizine-1241
Evstigneeva, R. P., L. V. Lavrova, Ts. D. Zarankina and N. A. Preobrazhenskii. Investigations in the Isoquinoline Series. XIII. Synthesis of 8-Methylemetine-1246
Evstigneeva, R. P., see Chen Chang-pai-3116

Fabrichnyi, B. P., I. F. Shalavina and Ia. L. Gol'dfarb. Synthesis of Amino Acids of Aliphatic Series from Thiophene Derivatives. III. Synthesis of ω-Amino Acids-2556
Fabrichnyi, B. P., see Gol'dfarb, Ia. L.-213
Fabritsy, A., and E. D. Venus-Danilova. An Investigation of the Conversions of Secondary-Tertiary α-Glycols of the Acetylene Series Under the Action of Mercury Salts. III. 2-Methyl-1,4-Diphenylbutyne-3-Diol-1,2-3255
Fabritsy, A., see Pavlova, L. A.-634

Faermark, V. S., see Iakubovich, A. Ia.-313
Farberov, M. L., and V. A. Speranskaia. Synthesis of β-Chloro-Substituted Alcohols and Their Conversions-2190
Favorskaia, I. A., E. M. Auvinen and Iu. P. Artsybashev. Homologs of Monovinylacetylene. VII. Dehydration of Secondary Acetylenic Alcohols-1832
Favorskaia, I. A., see Artsybasheva, Iu. P.-3266
Favorskaia, T. A., and O. V. Sergievskaia. The Mechanism of the Dehydration of γ-Glycols. V. Study of the Properties and Transformations of the Acetylenic γ-Glycol-3-Methyl-1-Hexyn-3,6-Diol-88
Favorskaia, T. A., and O. V. Sergievskaia. The Mechanism of Dehydration of γ-Glycols. VI. Study of the Dehydration of 3-Methylhexyne-1-Diol-3,6-3260
Fedorova, I. P., see Kiprianov, A. I.-994
Fedorova, V. V., and P. G. Sergeev. Liquid-Phase Oxidation of Alkylaromatic Hydrocarbons with Atmospheric Oxygen. Oxidation of p-Cymene and p-sec-Butyltoluene-2581
Fedorova, V. V., and P. G. Sergeev. Liquid-Phase Oxidation of Alkaromatic Hydrocarbons by Atmospheric Oxygen. Oxidation of p-Di-Sec-Butylbenzene-2586
Fedotova, O. Ia., and M. A. Askarov and L. N. Sedov. Synthesis and Investigation of Poly-3,3'-Dimethyldiphenylmethaneadipo-N,N'-Diethylamide 753
Ferkhim, A. A., see Glagoleva, A. A.-285
Feshchenko, N. G., see Kirsanov, A. V.-336
Feshchenko, N. G., see Kirsanov, A. V.-1020
Fialkov, Iu. Ia., see Udovenko, V. V.-791
Finkel'shtein, A. I., see Roginskaia, Ts. N.-2266
Fioshin, M. Ia., and L. I. Kazakova. Synthesis of Lead Tetraacetate by Electrochemical Oxidation of Lead Diacetate at the Anode-2043
Fol'mov, V. P., and Z. P. Malevannaia. Addition of Organomagnesium Compounds to Isopropylidenemalonic Ester-3106
Frankovskii, Ch., see Porai-Koshits, B. A.-902
Frankovskii, Ch., see Porai-Koshits, B. A.-908
Frenkel', R. I., see Bruker, A. V.-2450
Fridman, S. G. Triaminopyridothiazole and the Products of Its Condensation with Dicarbonyl Compounds-3109
Frunze, P. M., see Korshak, V. V.-2039
Funke, V. F., and G. V. Samsonov. The Preparation and Certain Properties of Silicon Nitride-269
Furshtatova, V. Ia., E. E. Mikhlina and M. V. Rubtsov. Synthesis of 6-Carboxymethyl-1-Azabicyclo[3,2,1] Octane-7-Carboxylic Acid and Some of Its Derivatives-650
Furshtatova, V. Ia., see Nikitskaia, E. S.-2810
Gaeva, L. A., see Dokunikhin, N. S.-2698
Gaeva, L. A., see Dokunikhin, N. S.-2974
Gal'bershtam, M. A., see Iur'ev, Iu. K.-602
Galegov, G. A., see Maimind, V. I.-2260
Gamper, N. M., see Kabachnik, M. I.-1618
Gavrilov, V. G., and M. I. Buzanov. Thermocatalytic Conversions of α-Methylnaphthalene-2750
Gavrilov, V. G., and S. A. Velichko. Effect of Preliminary Thermal Destruction on the Oxidizability of Methane Hydrocarbons-2138
Gavrilov, N. I., see Akimova, L. N.-391
Gavrilova, A. I., see Sergievskaia, S. I.-1884
Gavrilova, A. I., see Sergievskaia, S. I.-1890
Gefter, E. L. Some Esters of γ-Chlorocrotyl Alcohol-486
Gefter, E. L. Improved Methods of Synthesis of Phenyldichlorophosphine and Phenylphosphinic Dichloroanhydride-1398
Gefter, E. L. An Improved Method of Synthesis of Di-β,β'-Chloroethyl Ester of β-Chloroethylphosphonic Acid-1949
Gefter, E. L. The Problem of Synthesis of Di-β,β'-Chloroethyl Ester of Vinylphosphonic Acid-2536
Geita, L. S., and G. Ia. Vanag. Compounds with Two Geminate Indandione Groups in the Molecule. II. Condensation of 5,6-Dinitroacenaphthenequinone with 1,3-Indandione-2825
Gel'fer, Ts. M., see Chlenova, R. S.-3006
Geller, B. A. A Study of the Mechanism of Diazoexchange in Azo Dyes of the Naphthalene Series Made by Means of the Heavy Nitrogen Isotope-1985
Gembitskii, P. A., see Levina, R. Ia.-2849
Gents, F., see Kost, A. N.-2796
Genusov, M. I., see Petrov, A. A.-1190
Genusov, M. L., see Petrov, A. A.-2171
Genusov, M. I., see Petrov, A. A.-3248
Gerasimenko, I. I., see Labenskii, A. S.-3150
Gerchuk, M. P., see Ridel', N. V.-1365
Ginsburg, V. A., and A. Ia. Iakubovich. Synthesis of Heteroorganic Compounds of the Aliphatic Series by the Diazo Method. VIII. Synthesis of Compounds of Group V Elements. Organophosphorus Compounds. Experiments on the Synthesis of Di- and Trihaloalkylphosphines and Some Reactions of Chloroalkyl Derivatives of Phosphorus-710
Ginsburg, V. A., and N. F. Privezentseva. Iodo Derivatives of Methylphosphine-716
Ginsburg, V. A., see Iakubovich, A. A.-1006
Ginsburg, V. A., see Iakubovich, A. Ia.-1002
Gintse, I. K., see Grigor'eva, N. E.-1730

Gintse, N. F., see Danilov, S. N.-2978
Gintse, N. F., see Danilov, S. N.-3221
Gintse, N. F., see Plisko, E. A.-3203
Ginzburg, O. F., see Kviat, E. I.-52
Gitis, S. S., and A. I. Glaz. Reactions of Aromatic Nitro Compounds. III. A New Method for the Preparation of Alkyl Ethers of 2,4-Dinitrophenol-1393
Gitis, S. S., M. S. Malinovskii and A. I. Glaz. Reactions of Aromatic Nitro Compounds. IV. Transalkylation of 2,4-Dinitrophenolic Ethers-2299
Giuli-Kevkhian, R. S., see Babaian, A. T.-1314
Gladshtein, B. M., V. N. Chernetskii, M. I. Kiseleva and L. Z. Soborovskii. Organic Sulfur Compounds. III. Properties of Haloalkane-, Alkene- and Haloalkenesulfonyl Fluorides-2145
Gladshtein, B. M., I. P. Kuliulin and L. Z. Soborovskii. Investigation of a Series of Organic Sulfur Compounds. IV. Synthesis of β-Chloroethanesulfonyl Chloride-2454
Gladshtein, B. M., see Soborovskii, I. Z.-1909
Gladshtein, B. M., see Soborovskii, I. Z.-1913
Glagoleva, A. A., and A. A. Ferkhim. A Study of Aqueous Solutions of Acetic Acid by the Method of Raman Spectra-285
Glaz, A. I., see Gitis, S. S.-1393
Glaz, A. I., see Gitis, S. S.-2299
Glukhov, N. A., M. M. Koton and Z. A. Koroleva. Synthesis and Study of the Polymerizability of Halogen-Substituted Styrene Derivatives. VII. Trichlorostyrene and Pentachlorostyrene-3303
Glushkov, R. G., see Evstigneeva, R. P.-2499
Glushkova, N. E., see Dolgov, B. N.-2737
Gluzman, M. Kh. Reactions Involving Organic Solids. XI. The Influence of Temperature on the Conversion of N-Arylamic Acids into Imides-3016
Godovikov, N. N., see Kabachnik, M. I.-1618
Godovikova, S. N., see Iur'ev, Iu. K.-2207
Godovikova, S. N., see Iur'ev, Iu. K.-2793
Gogdanova, L. P., see Gorin, Iu. A.-1205
Gol'dfarb, Ia. L., B. P. Fabrichnyi and I. F. Shalavina. Synthesis of Aliphatic Amino Acids from Thiophene Derivatives. II. Synthesis of β-Amino Acids-213
Gol'dfarb, Ia. L., see Fabrichnyi, B. P.-2556
Golodnikov, G. V., B. N. Dolgov and L. N. Propp. Catalytic Preparation of Ketones from a Mixture of n-Butyric Acid and Ethyl Alcohol-2134
Golovanova, T. G., see Blidin, V. P.-2955
Golubtsov, S. A., see Andrianov, K. A.-330
Gonadze, G. M., see Nogaideli, A. I.-895
Gorbacheva, I. N., L. P. Varnakova, E. M. Kleiner, I. I. Chernova and N. A. Preobrazhenskii. Synthesis of Racemic Methyl Ether of O,O-Dibenzylmagnoline-167
Gorban', A. K., see Shostakovskii, M. F.-2862
Gorebenko-Germanov, D. S., see Iakovlev, G. N.-2653
Gorenbein, E. Ia., and V. N. Danilova. Investigation of Complex-Formation in Solutions of Ternary Systems by Physicochemical Analysis Methods. IX. The systems $AlBr_3$-(iso-C_5H_{11})$_2$O-C_6H_5Br and $AlBr_3$-(iso-C_5H_{11})$_2$O-C_6H_5Cl-1445
Gorgan, A. K., see Shostakovskii, M. F.-2864
Gorin, Iu. A., and L. P. Bogdanova. Investigation in the Field of Vapor-Phase Catalytic Hydration of Acetylene and Its Derivatives. I. Hydration of Vinylacetylene to Methylvinyl Ketone-640
Gorin, Iu. A., and L. P. Bogdanova. Investigation of the Vapor-Phase Catalytic Hydration of Acetylene and Its Derivatives. II. Hydration of Ethynylbenzene, Tert- Butylacetylene, Dimethylacetylene, Methylethylacetylene and Ethylvinylacetylene-1205
Gorin, Iu. A., and I. K. Gorn. The Vapor-Phase Catalytic Hydration of Acetylene and Its Homologs. III. Study of the Process of Catalytic Hydration of Acetylene Over Some Solid Catalysts-2366
Gorin, Iu. A., and V. S. Ivanov, E. S. Bogdanova and E. A. Piaivinen. Diene Hydrocarbons from Unsaturated Alcohols. I. Catalytic Dehydration of Crotyl Alcohol to Butadiene-170
Gorin, Iu. A., V. S. Ivanov and E. K. Khrennikova. Diene Hydrocarbons from Unsaturated Alcohols. II. Catalytic Dehydration of Tiglyl Alcohol and 2-Ethylhexene-2-ol to Diene Hydrocarbons-1474
Gorn, I. K., see Gorin, Iu. A.-2366
Gornostaeva, S. E., see Ushenko, I. K.-1717
Gorovits, M. B., see Abubakirov, N. K.-2316
Gottikh, B. P., see Kochetkov, N. K.-1559
Gottikh, B. P., see Kochetkov, N. K.-2759
Grachev, I. V., see Baranchik, N. M.-1400
Gracheva, E. P., see Shostakovskii, M. F.-1308
Gracheva, E. P., see Shostakovskii, M. F.-2379
Gracheva, E. P., see Shostakovskii, M. F.-2382
Gracheva, R. A., see Terent'ev, A. P.-1225
Grad, N. M., see Kaplan, S. Z.-3310
Grad, N. M., see Plisko, E. A.-3203
Gramenitskaia, V. N., see Petrov, A. D.-2353
Grandberg, I. I., and A. N. Kost. Reactions of Hydrazine Derivatives. XX. Dehydrogenation of Pyrazolines-3102
Grandberg, I. I., see Kost, A. N.-503
Grebeniuk, A. D., and I. P. Tsukervanik. Condensation of γ,γ,γ-Trichlorocrotononitrile with Benzene in the Presence of Aluminum Chloride-2417
Grigor'eva, N. E., and I. K. Gintse. Monoanils of Glutaconic Aldehyde. II. Effect of the Medium on

the Color of Derivatives of Primary Aromatic Amines-1730

Grigor'eva, N. E. and A. A. Pechka. Monoanils of Glutaconic Aldehyde. I. Derivatives of Primary Aromatic Amines-1726

Grinenko, G. S., and V. I. Maksimov. Investigation of the Synthesis of Steroid Hormone Analogs. III. Preparation of 3-(p-Methoxyphenyl)-Δ^2-Cyclopenten-1-One-1-Acetic Acid-519

Grinenko, G. S., and V. I. Maksimov. Investigations in the Field of Analogs of Steroid Hormones. IV. Catalytic Hydrogenation of 3-(p-Methoxyphenyl)-Δ^2-Cyclopenten-1-One-2-Acetic Acid-522

Grinenko, G. S., see Maksimov, V. I.-2218

Grinenko, G. S., see Maksimov, V. I.-2222

Grinev, A. N., and A. P. Terent'ev. Investigations on Quinones. XX. Preparation of Naphthoquinones and Dihydroanthraquinones-77

Grinev, A. N., and A. P. Terent'ev. Investigation on Quinones. XXI. The Structure of Substances Prepared by Condensation of Toluquinone and α-Naphthoquinone with Ethyl Acetoacetate-80

Grinev, A. N., N. K. Venevtseva and A. P. Terent'ev. The Alkylation of Substituted 5-Hydroxybenzofurans; Synthesis of New Plant Growth Stimulants -1894

Grinev, A. N., N. K. Venevtseva,and A. P. Terent'ev. Studies in the Field of Quinones. XXIII. Studies of the Condensation of p-Benzoquinone and 2,3-Dichloroquinone with Acetoacetic Ester and Its Analogs-1900

Grinev, A. N., I. A. Zaitsev, V. I. Shvedov and A. P. Terent'ev. Investigations on Quinones. XXII. The Synthesis of Substituted Indoles-439

Grinev, A. N., I. A. Zaitsev, N. K. Venevtseva and A. P. Terent'ev. A New Method for Obtaining Substituted Benzofurans and Indoles from Esters of Benzofuran and Indole-β-carboxylic Acids-1897

Grishchuk, A. P., and Baranov, S. N. Synthesis and Reactions of Some Thiazolidine Derivatives. I. Preparation of Azorhodanines-869

Grishko, N. I., and E. N. Gur'ianova. Isotopic Exchange of Sulfur in Salts of Organic Thiosulfonic Acids-1345

Gruz, B. E., see Iagupol'skii, L. M.-1656

Gudrinietse, E. Iu., A. F. Ievin'sh and G. Ia. Vanag. Sulfonation of β-Diketones with Dioxane Sulfotrioxide. II. Indandione-1,3-Sulfonic-2 Acid and Its Salts-95

Gudrinietse, E. Iu., and G. Ia. Vanag. Investigations of Cyclic Arylazo-β-Diketones. I. Condensation of 1,3-Indandiol with Diazo Compounds-59

Gudrinietse, E. Iu., see Neiland, O. Ia.-1256

Gunar, V. I., see Nazarov, I. N.-1498

Gura, D. V., see G. I. Bazilevskaia-1065

Guretskii, I. Ia., see Kreshkov, A. P.-188

Gurevich, A. I. Decarboxylation of Acridine-9-Carboxylic Acids with Carbonyl-Containing Compounds-318

Gur'ianova, E. N. Discussion. Concerning the Papers of L. M. Litvinenko, R. S. Cheshko, S. V. Tsukerman, A. D. Gofman, B. M. Kolesnikova and Others on "Spatial Structure and Reactivity."-816

Gur'ianova, E. N., and L. A. Egorova. Accelerating Effect of Amines on Isotope Exchange of Sulfur in Organic Polysulfides-1794

Gur'ianova, E. N., see Grishko, N. I.-1345

Gusev, B. P., see Nazarov, I. N.-1498

Iablochnik, N. S., see Shpital'nyi, A. S.-3307

Iagupol'skii, L. M., and R. V. Belinskaia. The Synthesis of Phenyldifluoroacetic Acid and Its Derivatives-750

Iagupol'skii, L. M., B. E. Gruz and A. I. Kiprianov. Synthesis of p-Nitrophenylhalogenomethyl Carbinols-1656

Iagupol'skii, L. M., and P. A. Iufa. The Interaction of Phenylphosphorus Tetrachloride with Diazomethane-2880

Iakhontov, L. N., S. V. Iatsenko and M. V. Rubtsov. Synthesis of Substituted Quinuclidine-2-Carbinols-1234

Iakhontov, L. N., S. V. Iatsenko and M. V. Rubtsov. The Synthesis of 4-Aminopiperidine-3146

Iakhontov, L. N., and M. V. Rubtsov. Reduction of Derivatives of Harmine with Sodium Borohydride to Derivatives of Py-tetrahydroharmine-3139

Iakhontov, L. N., see Nikitskaia, E. S.-2810

Iakobson, G. G., see Vorozhtsov, N. N., Jr.-40

Iakovlev, G. N., D. S. Gorbenko-Germanov, R. A. Zenkova, V. M. Razbitnoi and K. S. Kazanskii. Study of Double Sulfates of Americium by Absorption Spectra in Crystals-2653

Iakovlev, I. P., and D. P. Popa. Catalytic Synthesis of Ketones. V. Synthesis of Methyl Phenyl, Ethyl Phenyl, Methyl n-Propyl, and Di-n-Propyl Ketones-2510

Iakovleva, E. A., see Shatenshtein, A. I.-1761

Iakovleva, T. V., see Petrov, A. A.-2357

Iakubchik, A. I., and N. N. Motovilova. The Structure of the Potassium-Divinyl (Butadiene) Polymer-413

Iakubchik, A. I., A. I. Spasskova and L. A. Shibaev. A Study of the Chemical Structure of Sodium-Carbonic Acid Polymers of Divinyl-2095

Iakubchik, A. I., A. I. Spasskova and V. A. Tsitokhtsev. A Study of the Chemical Structure of the Spongy Divinyl Polymer. II-143
Iakubchik, A. I., A. I. Spasskova and B. I. Tikhomirov. The Abnormal Products of Vinyl-1-Cyclohexene-3 Ozonolysis-890
Iakubchik, A. I., A. I. Spasskova, A. G. Zak and I. D. Shostatskaia. Comparative Study of Chemical Structure of SKB Rubber and SKBM Rubber by the Method of Ozonolysis-3121
Iakubovich, A. A., S. P. Makarov and V. A. Ginsburg. A Method of Obtaining Fluorine Derivatives of Silicon, Tin and Sulfur-1006
Iakubovich, A. Ia., N. A. Bogoslovskii, E. P. Pravova and S. M. Rozenshtein. Syntheses of Vinyl Monomers. IV. Fluorine-Substituted Acrylates-2325
Iakubovich, A. Ia., and V. A. Ginsburg. The Reaction of Hydrazine with Carbon Disulfide. Experiments on the Synthesis of Diisothiocyanogen-1002
Iakubovich, A. Ia., V. V. Razumovskii and I. N. Beliaeva. Synthesis of Vinyl Monomers. III. Synthesis of Compounds with a Carbonyl Group-660
Iakubovich, A. Ia., E. P. Pravova and N. A. Bogoslovskii. Synthesis of Vinyl Monomers. II. Some Derivatives of α-Chloroacrylic Acid-316
Iakubovich, A. Ia., V. V. Razumovskii, Z. N. Vostrukhina and S. M. Rozenshtein. Synthesis of Vinyl Monomers. III. Concerning the Syntheses of Vinyl Esters from Aceto- and Chloromercuriacetaldehydes and Concerning the Mechanism of these Reactions-1971
Iakubovich, A. Ia., V. Razumovskii and S. Rozenshtein. Synthesis of Vinyl Monomers. V. Syntheses of Cyano-Substituted Acrylates-2329
Iakubovich, A. Ia., L. Z. Soborovskii, L. I. Muler and V. S. Faermark. Synthesis of Vinyl Monomers. I. α-Substituted Derivatives of Vinylphosphonic Acid-313
Iakubovich, A. Ia., see Ginsburg, V. A.-710
Iakubovich, A. Ia., see Motsarev, G. V.-1395
Iakubovich, A. Ia., see Motsarev, G. V.-2754
Iarmukhamedova, E. Sh., and T. N. Sumarokova. Complex Compounds of Stannic Chloride and Bromide with Urea-1468
Iarovenko, N. N. Properties of Heteroorganic Compounds in the Light of D. I. Mendeleev's Periodic System. I. Boiling Points of Compounds of Fluorine and Other Halogens-2543
Iarovenko, N. N., and S. P. Motornyi. Preparation of Esters of N-Trifluoromethylthiolcarbamic Acid-2541
Iarovenko, N. N., and A. S. Vasil'eva. A New Method of Introduction of Trihalomethyl Group into Organic Compounds-2539
Iashunskii, V. G. Substances with Complex Forming Ability. II. Trans-1,2-Diaminocyclopentane-N,N,N',N'-Tetraacetic Acid and Trans-1,2-Diaminocyclobutane-N,N,N',N'-tetraacetic Acid-1026
Iashunskii, V. G. Substances Capable of Complex Formation. III. Cis-1,2-Diaminocyclohexane--1420
Iashunskii, V. G., and M. N. Shchukina. Substances Capable of Forming Complexes. I. Synthesis and Structure of "Complexon-IV"-1,2-Diaminocyclohexane-N,N,N',N'-tetraacetic Acid-230
Iatsenko, S. V., see Iakhontov, L. N.-1234
Iatsenko, S. V., see Iakhontov, L. N.-3146
Idel'chik, Z. B., and V. I. Pansevich-Koliada. Investigation of Oxido Compounds. X. Reaction of α-Oxides of Allyl Ethers of Phenol, o- and p-Cresols and Guaiacol with Amines-770
Idel'chik, Z. B., see V. I. Pansevich-Koliada-887
Ievin'sh, A. F., see Bankovskii, Iu. A.-2310
Ievin'sh, A. F., see Gudrinietse, E. Iu.-95
Ioffe, B. V. Synthesis of Unsymmetrical Dialkylhydrazines-1354
Ioffe, D. V., see Rachinskii, F. Iu.-3027
Iufa, P. A., see Iagupol'skii, L. M.-2880
Iurkevich, A. M., A. V. Dombrovskii and A. P. Terent'ev. Haloarylation of Unsaturated Compounds by Aromatic Diazo Compounds. X. Synthesis of DL-Phenylalanine and Its Homologs-226
Iushina, L. D. The Electrolytic Reduction of Thorium Tetrachloride in Salt Melts-274
Iur'ev, Iu. K., and Z. V. Beliakova. Tetraacyloxysilanes in Organic Synthesis. XII. Synthesis of N,N-Diethylamides and N-Arylamides of Acids with the Aid of Silicoanhydrides of Saturated Monobasic Organic Acids-1
Iur'ev, Iu. K., and Z. V. Beliakova. Tetraacyloxysilanes in Organic Synthesis. XVI. Benzoyloxytrichlorosilane and Reactivity of Benzoyloxy Group-1803
Iur'ev, Iu. K., Z. V. Beliakova and V. P. Volkov. Tetraacyloxysilanes in Organic Synthesis. XVII. Acylation of Benzene with the Silicoanhydrides of Acetic, Mono-, Di- and Trichloroacetic and β-Bromopropionic Acids-2408
Iur'ev, Iu. K., and Z. V. Beliakova and G. B. Eliakov. Tetraacyloxysilanes in Organic Synthesis. XVII. Structure of the Silicoanhydrides of Dibasic Saturated Organic Acids-2789
Iur'ev, Iu. K., and S. V. Diatlovitskaia. Ethylene Sulfide in the Synthesis of Heterocyclic Compounds with Two Hetero Atoms. VIII. Synthesis of 2-(2-Furyl)-, 2-(2-Thienyl)-, and 2-(2-Selenienyl)-3-arylthiazolidines-2413

Iur'ev, Iu. K., and G. B. Eliakov and A. N. Vysokosov. Tetracyloxysilanes in Organic Synthesis. XIV. Synthesis of Homologs of Cinnamic Acid (α-Alkyl-β-Phenylacrylic Acids)-1361

Iur'ev, Iu. K., G. B. Eliakov and A. N. Vysokosov. Tetraacyloxysilanes in Organic Synthesis. XV. Synthesis of α,β-Unsaturated Acids of the Furan and Thiophene Series-1603

Iur'ev, Iu. K., and S. V. Kiatlovitskaia. Ethylene Sulfide in the Synthesis of Heterocyclic Compounds with Two Hetero-Atoms. VII. 3-Arylthiazolidine-2-Carboyxlic Acids and Their Derivatives-848

Iur'ev, Iu. K., and N. V. Makarov. 1,4-Hydroxyketones and 1,4-Diketones in the Catalytic Synthesis of Homologs of Δ^2-Pyrroline and Δ^2-Dihydrothiophene, and Corresponding Homologs of Pyrrole and Thiophene-857

Iur'ev, Iu. K., and N. N. Mezentsova. Chemistry of Selenophene. XIV. Reactions of Selenophene-2-Aldehyde-3071

Iur'ev, Iu. K., and N. N. Mezentsova and V. E. Vas'kovskii. Chemistry of Selenophene. XV. 2-Vinylselenophene-3288

Iur'ev. Iu. K., E. G. Rozantsev and S. N. Godovikova. The Synthesis of 2,5-Dimethyl-3-alkylfuranidines-2207

Iur'ev, Iu. K., N. K. Sadovaia and M. A. Gal'bershtam. Chemistry of Selenophene. X. Synthesis of 3-Methylselenophene-2-Aldehyde and 2,3- and 2,4-Dimethylselenophene-602

Iur'ev, Iu. K., and N. K. Sadovaia. The Chemistry of Selenophene. XI. α-Iodoselenophenes in the Organomagnesium Synthesis of Selenophene-α-carboxylic Acids-2200

Iur'ev, Iu. K., N. K. Sadovaia and V. V. Titov. Chemistry of Selenophene. XIII. Cyanoethylation of Ketones of the Selenophene Series-3066

Iur'ev, Iu. K., A. N. Vysokosov and S. N. Godovikova. Tetraacyloxysilanes in Organic Synthesis. XIX. Synthesis of 3- and 4-Nitrocinnamic Acids and Their Homologs [α-Alkyl-β-(nitrophenyl)acrylic Acids]-2793

Iur'ev, Iu. K., and E. L. Zaitseva. The Chemistry of Selenophene. XII. 5-Nitroselenophene-2-aldehyde and 5-Nitroselenophene-2-carboxylic Acid-2203

Iur'ev, Iu. K., and I. G. Shukova. Catalytic Conversions of Heterocyclic Compounds. LIII. Conversion of Homologs of Oxazole to Homologs of Thiazole-5

Ivanov, S. S., and M. M. Koton. Synthesis Properties and Polymerization of α-Chloroacrylamide-139

Ivanov, S. S., and M. M. Koton. On the Reaction of Ammonia with Methyl α-Chloroacrylate-644

Ivanov, V. S., see Gorin, Iu. A.-170

Ivanov, V. S., see Gorin, Iu. A.-1474

Ivanova, N. G., see Motsarev, G. V.-1395

Ivanova, V. N. I. Nitrogen Compounds of Phenylated Derivatives of Thiophene-1288

Ivanova, V. N. The Absorption Spectra of α- and β-Phenylthiophenes and Their Nitro Derivatives. II-1293

Ivin, S. Z. Reaction of Alkylene Sulfides with Halides of Carboxylic Acids-177

Ivin, S. Z., Reaction of Halides of Carboxylic Acids with Aliphatic α-Oxides-181

Ivin, S. Z., On the Synthesis of Choline and Thiocholine Esters of Carboxylic Acids-1390

Ivin, S. Z., and K. V. Karavanov. Reactions of Sulfur and Inorganic Sulfides with Dialkyltrichlorophosphine-Aluminum Chloride Adducts-2988

Ivin, S. Z., see Komkov, I. P.-2990

Ivin, S. Z., see Komkov, I. P.-2992

Izrailevich, E. A., see Shatenshtein, A. I.-2969

Kabachnik, M. I., N. N. Godovikov, D. M. Paikn, M. P. Shabanova, N. M. Gamper and L. F. Efimova. Organophosphorus Insecticides. Some Derivatives of Methylthiophosphonic and Methyldithiophosphonic Acids-1618

Kabachnik, M. I., see Mastriukova, T. A.-1613

Kachurgin, O. I., see Spryskov, A. A.-2250

Kachurgin, O. I.,see Spryskov, A. A.-1693

Kagramanova, G. B., see Babak, S. F-1312

Kaikaris, P. S., see Levina, R. Ia.-2347

Kaikaris, P. A., see Levina, R. Ia.-2849

Kamai, Gil'm, and V. A. Kukhtin. Addition of Neutral Esters of Phosphorous and Phosphonous Acids to Conjugated Systems. IV. Addition of Esters of Phenylphosphonous Acid to α,β-Unsaturated Aldehydes and Acids-913

Kamai, Gil'm., see Kukhtin, V. A.-1252

Kamernitskii, A. V., see Nazarov, I. N.-1511

Kamernitskii, A. V., see Nazarov, I. N.-1850

Kaplan, E. P., see Egorov, Iu. P.-3284

Kaplan, E. P., see Petrov, A. D.-589

Kaplan, S. Z., N. M. Grad and A. S. Zvontsova. N-Alkylated and N-Aralkylated Morpholine Derivatives-3310

Karapetian, M. G., see Shemiakin, M. M.-2107

Karavanov, K. V., see Ivin, S. Z.-2988

Karavanov, K. V., see Komkov, I. P.-2990

Karavanov, K. V., see Komkov, I. P.-2992

Karishin, A. P., and D. M. Kustol. Synthesis of Naphthalimide and Its Derivatives-673

Karpeiskii, M. Ia., see Kochetkov, N. K.-3042

Karpinskii, V. S., see Dashkevich, L. B.-3040

Karpov, V. I., see M. M. Shemiakin-952

Kashirskii, M. I., see Abramov, V. S.-3090

Kashnikova, N. M., see Evstigneeva, R. P.-1241
Kastron, Ia. A., see Martynov, V. F.-2119
Kazakova, L. I., see Fioshin, M. Ia.-2043
Kazanskaia, V. F., see Tishchenko, V. V.-2313
Kazanskii, K. S., see Iakovlev, G. N.-2653
Khaletskii, A. M., V. G. Pesin and Chou Ts'in. Synthesis and Study of N-Oxides of Heterocyclic Compounds. I. N-Oxide Derivatives of Morphine, Tetrahydroisoquinoline and Quinoline-2386
Khaletskii, A. M., V. G. Pesin and Chou Ch'ing. Synthesis and Investigation of N-Oxides of Heterocyclic Compounds. II. N-Oxides of Acridine Derivatives-2845
Khaletskii, A. M., V. G. Pesin and Teng Jun-hsiang. Chemistry of Pyrazolidine. I. Synthesis and Study of Some Mono- and Disubstituted Derivatives of 1,2-Diphenyl-3,5-dioxypyrazolidine-2393
Khaletskii, A. M., V. G. Pesin and Teng Jun-hsiang. Chemistry of Pyrazolidine. II. Study of the Reactivity of 1,2-Diphenyl-3,5-Dioxopyrazolidine (nitration, sulfonation, etc.)-3057
Khaletskii, A. M., see Pesin, V. G.-20
Khaletskii, A. M., see Pesin, V. G.-378
Khaletskii, A. M., see Pesin, V. G.-2126
Khaletskii, A. M., see Pesin, V. G.-2131
Khaletskii, A. M., see Pesin, V. G.-2841
Khaletskii, A. M., see Pesin, V. G.-3060
Khaletskii, A. M., see Pesin, V. G.-3300
Khananashvili, L. M., see Kreshkov, A. P.-2150
Kharit, Ia. A., see Shpital'nyi, A. S.-2715
Kharitonov, N. P., see Dolgov, B. N.-2737
Kharitonov, N. P., see Dolgov, B. N.-2741
Khenokh, M. A., and E. M. Lapinskaia. Change in Proteins and Amino Acids Under the Influence of Ultrasonic Vibrations-658
Khenokh, M. A., and E. M. Lapinskaia. Action of γ-Radiation of Radioactive Cobalt (Co^{60}) on Aqueous Solutions of Aromatic Hydrocarbons-679
Kheruze, Iu. I., see Petrov, A. A.-1490
Khlopin, N. Ia., and G. F. Reikhardt. Determination of the Number of Electrons Participating in the Process for the Reduction of Stypticine at a Dropping Mercury Electrode. II-266
Khmelevskii, V. I., and E. I. Abramova. Synthesis of Theophylline and Caffeine from Urea and Sodium Cyanoacetate-2012
Khmelevskii, V. I., E. I. Abramova and L. V. Variukhina. Preparation of Theophylline and Caffeine from Uric Acid-2016
Khmel'nitskii, L. I., S. S. Novikov and O. V. Lebedev. Reaction of Nitrogen Tetroxide with Organic Compounds. II. Reaction of Nitrogen Tetroxide with Aci-Phenylnitromethane and Its Salt-2340
Khmel'nitskii, L. I., see Novikov, S. S.-2333
Khmel'nitskii, L. I., see Novikov, S. S.-2342
Khokhlov, D. N., see Kutepov, D. F.-663
Khomiakov, V. G., S. S. Kruglikov and V. M. Berezovskii. Electrosynthesis of Nicotinic Acid-2925
Khomutov, R. M., see Kochetkov, N. K.-3042
Khomutova, E. D., see Kochetkov, N. K.-356
Khomutova, E. D., see Kochetkov, N. K.-2762
Khorlin, A. I., O. S. Chizhov and N. K. Kochetkov. Derivatives of Bicyclo(1,2,2)Heptane. IV. Some Amines and Aminoalcohols of the Bicyclo(1,2,2) Heptane Series-3370
Khorlin, A. Ia., see Kochetkov, N. K.-1977
Khrennikova, E. K., see Gorin, Iu. A.-1474
Khrennikova, E. K., see Tiniakova, E. I.-1682
Khrennikova, E. K., see Tiniakova, E. I.-3295
Khromov-Borisov, N. V., see Torf, S. F.-2488
Khudobin, Iu. I., see Dolgov, V. N.-2737
Khydyrov, D., see Shamkhal Mamedov-2836
Kiatlovitskaia, S. V., see Iur'ev, Iu. K.-848
Kikharskaia, E. V., see Korshak, V. V.-2039
Kikiforova, N. M., see Bruker, A. B.-2445
Kiprianov, A. I., and I. P. Fedorova. Azo Derivatives of Cyanine Dyes-994
Kiprianov, A. I., see Babichev, F. S.-209
Kiprianov, A. I., see Iagupol'skii, L. M.-1656
Kirsanov, A. V., G. I. Derkach and R. G. Makitra. Triaroxyphosphazoacyls-1283
Kirsanov, A. V., and G. I. Derkach. Trichloroisophosphazoacyls of the Aromatic Series-1930
Kirsanov, A. V., and G. I. Derkach. Triaroxyisophosphazoacyls of Aromatic Series-2283
Kirsanov, A. V., and N. L. Egorova. Triaryloxyphosphazosulfonalkyls and Aromatic Esters of Alkyl Sulfonamidophosphoric Acids-1023
Kirsanov, A. V., and N. L. Egorova. Anilides of Alkylsulfonamidophosphoric Acids-1636
Kirsanov, A. V., and N. G. Feshchenko. Trimethoxy- and Triaryloxyphosphazosulfonitrophenyls and Diesters of Nitrophenylsulfonamidophosphoric Acids-336
Kirsanov, A. V., and N. G. Feshchenko. Esters of Aminophenylsulfonamidophosphoric Acid-1020
Kirsanov, A. V., and E. S. Levchenko. Salts of the Acid Fluorides of Arylsulfonamidophosphoric Acids-1639
Kirsanov, A. V., and R. G. Makitra. Diesters of Arylamidophosphoric Acids-35
Kirsanov, A. V., and L. L. Matveenko. Bis-Triaryloxyphosphazo-Sulfones and Tetraaryl Esters of Sulfamidobisphosphoric Acid-1935
Kirsanov, A. V., and V. P. Molosnova. The Reaction of Phosphorus Pentachloride with Esters of Oxamic Acid. Amides of Alkoxydichloroacetic Acids-31
Kirsanov, A. V., and V. P. Molosnova. Trichlorophosphazoaryloxydichloroacetyls-344

Kirsanov, A. V., and Z. D. Nekrasova. Diphenylamides of Trichlorophosphazocarbonic Acids and Their Derivatives-1644
Kirsanov, A. V., and I. N. Zhmurova. Reaction of Phosphorus Pentachloride with Amides of Phosphoric Acid-2514
Kirsanov, A. V., and Iu. M. Zolotov. Substituted Imido- and Monoarylsulfamides-340
Kiseleva, M. I., see Gladshtein, B. M.-2145
Kiseleva, M. I., see Soborovskii, L. Z.-1909
Kiseleva, M. I., see Soborovskii, L. Z.-1913
Kiseleva, T. M., see Koton, M. M.-409
Klebanskii, A. L., and D. M. Krasinskaia. The Synthesis of Alkoxy Derivatives of Divinylacetylene. VII. The Direction of Addition of Ethyl Alcohol to Divinylacetylene-2100
Klebanskii, A. L., A. G. Saiadian and M. G. Barkhudarian. Investigation of the Mechanism of Polycondensation of 1,3-Dichlorobutene-2 in the Presence of Friedel-Crafts-Gustavson Catalysts. I-554
Klebanskii, A. L., A. G. Saiadian and M. G. Barkhudarian. Interaction of 1,3-Dichlorobutene-2 with Chloroprene Under the Influence of Friedel-Crafts-Gustavson Catalysts. II-559
Klebanskii, A. L., A. G. Saiadian and M. G. Barkhudarian. Reaction of 1,3-Dichlorobutene-2 with Isoprene and Divinyl Under the Influence of FeCl$_3$. III-853
Klebanskii, A. L., A. G. Saiadian and A. G. Barkhudarian. Telomerization of Chloroprene in the Reaction with 1,3-Dichlorobutene-2 Under the Action of FeCl$_3$. IV-3279
Klebanskii, A. L., and M. S. Vilesova. Studies in the Field of Synthesis and Polycondensation of N-Alkyl Derivatives of Hexamethylenediamine. I. Synthesis of N,N'-Dialkyl Derivatives of Hexamethylenediamine-1036
Klebanskii, A. L., and M. S. Vilesova. Research in the Field of Synthesis and Polycondensation of N-Alkyl Derivatives of Hexamethylenediamine. II. The Synthesis of N-Monoalkyl Derivatives of Hexamethylenediamine-1042
Klebanskii, A. L., and M. S. Vilesova. Synthesis and Polycondensation of N-Alkyl Derivatives of Hexamethylenediamine. III. Influence of the Structure of the Substituting Radical and the Direction of Alkylation of Hexamethylenediamine-1574
Klebanskii, A. L., and M. S. Vilesova. Synthesis of N-Alkyl Derivatives of Hexamethylenediamine and Their Polycondensation. IV. Some Problems of the Kinetics of the Reductive Alkylation of Hexamethylenediamine-1578
Klebanskii, A. L., and M. S. Vilesova. Research in the Field of Synthesis and Condensation of N-Alkyl Derivatives of Hexamethylenediamine. V. Reaction Mechanism of Reductive Alkylation of Hexamethylenediamine-1815
Klebanskii, A. L., and M. S. Vilesova. Research in the Field of Synthesis and Condensation of N-Alkyl Derivatives of Hexamethylenediamine. VI. Synthesis of Polyamides Starting with N-Alkylated Hexamethylenediamine. Production of Partly N-Alkylated Polyamides-1820
Klebanskii, A. L., and M. S. Vilesova. A Study in the Field of Synthesis of N-Alkyl Derivatives of Hexamethylenediamine and Their Polycondensation. VII. Preparation of Completely N-Alkylated Polyamides and Coupling of Their Chains with a Diisocyanate-1824
Kleiner, E. M., see Gorbacheva, I. N.-167
Kleiner, K. E., and A. Kh. Klibus. The Reaction Between Sodium Tungstates and Stilbene-4,4'-bis-[(azo-1)-3,4-dihydroxybenzene]2,2'-disulfonic Acid ("Stilbazo") in Aqueous Solutions-2052
Klibus, A. Kh., see Kleiner, K. E.-2052
Klochikhin, A. A., see Maslov, P. G.-811
Kochetkov, N. K., Ivan Ambrush, T. I. Ambrush and E. S. Severin. Synthesis of Aliphatic β-Chlorovinyl Ketones from Hydroxymethylene Ketones-3053
Kochetkov, N. K., and N. V. Dubykina. Some N-ω-Phenylalkyl-β-Chloropropionamides-2437
Kochetkov, N. K., B. P. Gottikh and L. I. Kudriashov. Interaction of β-Chlorovinyl Ketones with β-Dicarbonyl Compounds. V. Ketovinylation of α-Alkyl Acetoacetic Esters-1559
Kochetkov, N. K., and B. P. Gottikh. Reaction of β-Chlorovinyl Ketones with β-Dicarbonyl Compounds. VII. Acid Cleavage of α-Alkyl-α-(3-ketoalkenyl)-acetoacetic Esters-2759.
Kochetkov, N. K., R. M. Khomutov, M. Ia. Karpeiskii and E. I. Budovskii. Cycloserine and Related Compounds. III. Synthesis of Cycloserine-3042
Kochetkov, N. K., and E. D. Khomutova. Isoxazole Derivatives. V. Substitution in 5-Phenylisoxazole-356
Kochetkov, N. K., E. D. Khomutova and M. V. Bazilevskii. Investigation in the Isoxazole Series. VII. Chloromethylation of Isoxazoles-2762
Kochetkov, N. K., and A. Ia. Khorlin. A Study in the Isoxazole Series. VI. Concerning the Synthesis of 3-Substituted Isoxazoles-1977
Kochetkov, N. K., and L. I. Kudriashov. Interaction of β-Chlorovinyl Ketone with β-Dicarbonyl Compounds. VI. Synthesis of some Derivatives of α-Pyrones-1562
Kochetkov, N. K., and L. I. Kudriashov. A New Reaction of α-Pyrones. Synthesis of Vinylogs of β-Oxo Acid Esters-3049
Kochetkov, N. K., see Khorlin, A. Ia.-3370

Kochetkov, N. K., see Kucherov, N. F.-2005
Kochetkov, N. K., see Kudriashov, L. I.-2009
Kochetkov, N. K., see Kudriashov, L. I.-2484
Kochetkov, N. K., and M. I. Petruchenko. Some β,β-Diarylethylamines-2288
Kochkin, D. A., see Shostakovskii, M. F.-2866
Kofman, Iu. I., see Boldyrev, B. G.-746
Kogan, L. M., N. M. Burmakin and N. V. Cherniak. The Chemistry of Processes of Far-Reaching Chlorination of Pentane-27
Kokhomskaia, V. V., see Bardyshev, I. I.-528
Kokhtin, V. A., and Gil'm Kamai. Addition of Full Esters of Phosphorous and Phosphinous Acids to Conjugated Systems. V. The Problem of the Mechanism of the Reaction of Trialkyl Phosphites with Conjugated Systems-1252
Kolesnikov, G. S., and L. I. Shcherbo. Derivatives of Hexamethylenimine. III. Substituted N-Benzylhexamethylenimines-509
Kologrivova, N. E., and V. N. Belov. Oxidation of α,β-Unsaturated Methyl Ketones with Sodium Hypobromite-1325
Kologrivova, N. E., and V. N. Belov. The Condensation of 1-Heptyne with Chloral-3136
Kolosov, M. N., see Shemiakin, M. M.-2107
Komkov, I. P., S. Z. Ivin and K. V. Karavanov. Reactions of Sulfur and Inorganic Sulfides with Aluminum Chloride Adducts of Alkyltetrachlorophosphine. -2990
Komkov, I. P., K. V. Karavanov and S. Z. Ivin. New Methods of Preparing Alkyldichlorophosphines and Dialkylchlorophosphines-2992
Kondrashov, I. A., and S. F. Babak. Compounds of Cadmium and Mercury Halides with Nicotine-1753
Konovalova, I. V., see Pudovik, A. N.-1263
Konshin, M. E., and P. A. Petiunin. Chemistry of Heterocycles. XXII. Di- and Polyhalo Derivatives of 9-Phenylacridine with Positions of Halogen in Different Benzene Rings-949
Koptiug, V. A., see Vorozhtsov, N. N.-368
Koptiug, V. A., see Vorozhtsov, N. N.-1697
Koptiug, V. A., see Vorozhtsov, N. N., Jr.-3010
Koretskaia, N. I., and L. M. Utkin. Alkaloids of *Peganum Harmala* L. II. The Structure of Two New Alkaloids-1056
Koroleva, Z. A., see Glukhov, N. A.-3303
Korol'kova, M. D., and B. K. Kricheviov. Physicochemical Analysis of the System Formic Acid-Dimethylformamide. Density, Viscosity, and Electrical Conductivity in the System Formic Acid-Dimethylformamide-2943
Korshak, V. V., P. M. Frunze, D. N. Andreev and E. V. Kukharskaia. About Properties of Polyamides with Siloxane Groupings-2039
Korshak, V. V., Mozgova, K. K., and Z. P. Zasechkina. The Effect of Low Molecular Weight Materials on the Photochemical Degradation of Polyethylene Terephthalate-2874
Korshunov, I. A., and N. F. Novotorov. Radiochemical Determination of the Number of Carbon Atoms in an Organic Molecule-48
Korshunov, I. A., and A. A. Orlova. Radiochemical Investigation of Reactions of Organometallic Compounds in Benzene Solution-45
Koshkin, N. V. Preparation of Disubstituted Amidines from Disubstituted Thioureas and Methylmagnesium Iodide-676
Kost, A. N., and F. Gents. Reactions of Hydrazine Derivatives. XIX. Condensation of 4-Amino-[1,2,4]-Triazole with Esters-2796
Kost, A. N., I. I. Grandberg and E. B. Evreinova. The Reactions of Hydrazine Derivatives. XVII. The Action of Acidic Reagents on Azines-503
Kost, A. N., see Grandberg, I. I.-3102
Kostenko, V. G., see Pigulevskii, G. V.-1471
Kostenko, V. G., see Pigulevskii, G. V.-1706
Kostin, V. N., see Levina, R. Ia.-3332
Kostsova, A. G. An Investigation in the Field of Alkanesulfonic Acids. XVI. Chlorination of Anisidides of Alkanesulfonic Acids.-1623
Kostsova, A. G., and N. T. Borisova. Investigation in the Field of Alkanesulfonic Acids. XVIII. Chlorination of Alkanesulfonic Acid Toluidides-2457
Koton, M. M., T. A. Sokolova, M. H. Savitskaia and T. M. Kiseleva. Cases of Hindered Polymerization of Monomers in the Aryl Methacrylate Series-409
Koton, M. M., see Glukhov, N. A.-3303
Koton, M. M., see Ivanov, S. S.-139
Koton, M. M., see Ivanov, S. S.-644
Kotrelev, V. N., and I. K. Rubtsova. The Reaction of Allyloxyethanol with Vinyl Ethers-748
Kotunenko, Z. Iu., see Malenok, N. M.-421
Kovner, M. L., see Sopov, N. P.-2184
Kozhin, S. A., see Pigulevskii, G. V.-1471
Kozhin, S. A., see Pigulevskii, G. V.-1706
Kozlov, N. S., and N. I. Panova. Catalytic Amination of Organic Compounds. VII. Catalytic Transformations in the Butylamine Series-2421
Kozlov, V. V., and I. K. Veselovskaia. Investigations in the Naphthalene Series. XVIII. On the Kinetics of Interactions of β-Naphthol with Aqueous Solutions of Ammonia and Ammonium Sulfite-3359
Koz'mina, O. P., V. I. Kurliankina, E. N. Matveeva and M. K. Aleksandrovich. The Formation of Peroxides in the Oxidation of Cellulose Ethers and Esters-3230

Krasinskaia, D. M., see Klebanskii, A. L.-2100
Krasnaia, Zh. A., see Nazarov, I. N.-451
Krasnaia, Zh. A., see Nazarov, I. N.-2477
Krasovitskii, B. M., R. M. Marskevich, N. A. Radochina, and K. P. Riazanova. Direct Azo Dyes-Derivatives of 1,8-Naphthoylene-1',2'-Benzimidazole-2520
Krasovskaia, T. A., see Andrianov, K. A.-330
Kravchenko, A. I., see Sergievskaia, S. I.-1884
Kremlev, M. M., see Kretov, A. E.-1991
Kremlev, M. M., see Kretov, A. E.-1995
Kreshkov, A. P., I. Ia. Guretskii and P. A. Andreev. Reaction of Some Organosilicon Compounds with Cellulose Nitrates.-188
Kreshkov, A. P., L. V. Myshliaeva and L. M. Khananashvili. Preparation of Organosilicon Hydroxy Compounds from Aminosilanes. I. Preparation of Alkylalkoxysilanes from Alkylphenylaminosilanes, Synthesized from Alkylchlorosilanes.-2150
Kretov, A. E., and Abrazhanova, E. A. Reaction of Arylsulfonamides with Propylene Oxide.-2802
Kretov, A. E., and M. M. Kremlev. Reaction of N,N-Dichlorobenzenesulfonamide with Polyhalogen Derivatives of Methane-1991
Kretov, A. E., and M. M. Kremlev. Reaction of N,N-Dichlorobenzenesulfonamide with Polyhalogen Derivatives of Methane-1995
Kretov, A. E., N. P. Romazanovich. Cyanoethylation of Aryl Sulfonamides-1029
Kretov, A. E., and G. V. Tikhonova. N-Arylsulfonamide Derivatives of Diethanolamine-2832
Kretsu, G., see Svetkin, Iu. V.-1907
Krichevlov, B. K., see Korol'kova, M. D.-2943
Krol', V. A., see Dolgov, B. N.-2433
Kropacheva, A. A., see Sventsitskaia, L. E.-1650
Kruglikov, S. S., see Khomiakov, V. G.-2925
Krupatkin, I. L. Investigation of Continuous Transitions from Stable into Metastable Phase Separation-800
Krupatkin, I. L. The Occurrence of Equilibrium of Three Liquid Phases in Ternary Systems.-1075
Krupina, G. P., see Maksimov, V. I.-2910
Krupina, G. F., see Maksimov, V. I.-2913
Kucherov, N. F., V. P. Evdakov and N. K. Kochetkov. Indole Derivatives. V. Synthesis of Bis-Quaternary Ammonium Salts of Harmine-2005
Kudriashov, L. I., and N. K. Kochetkov. β-Aminovinyl Ketones. IX. Salts of Trialkyl-(γ-oxoalkenyl)-Ammonium as Oxovinylating Agents-2009
Kudriashov, L. I., and N. K. Kochetkov. Synthesis of Dienic Acids from α-Pyrones-2484
Kudriashov, L. I., see Kochetkov, N. K.-1559
Kudriashov, L. I., see Kochetkov, N. K.-1562
Kudriashov, L. I., see Kochetkov, N. K.-3049
Kukalenko, S. S., and N. N. Mel'nikov. Organic Insectofungicides. XXVIII. The Synthesis of Some Esters of Bicyclo-(2,2,1)-heptenyl-5-carbinol-2.-153
Kukalenko, S. S., and N. N. Mel'nikov. Organic Insectofungicides. XXIX. The Reaction of Hexachlorocyclopentadiene with Some Unsaturated Compounds-157
Kukalenko, S. S., N. N. Mel'nikov, T. I. Naryshkina. Organic Insectogundicides. XXXIII. The Synthesis of Some Derivatives of 4,7-Endomethylenetetrahydroindan-471
Kukhareva, L. V., see Lebedeva, A. I.-2806
Kukhtin, V. A., and K. M. Orekhova. Addition of Neutral Esters of Phosphorous and Phosphonous Acids to Conjugated Systems. VI. Joint Reaction of Alkyl Halides and α,β-Unsaturated Acids with Trialkyl Phosphites-2814
Kukhtin, V. A., see Gil'm Kamai-913
Kulakova, V. N., see Zinov'ev, Iu. M.-1600
Kul'bovskaia, N. K., see Shostakovskii, M. F.-1308
Kul'bovskaia, N. K., see Shostakovskii, M. F.-2379
Kul'bovskaia, N. K., see Shostakovskii, M. F.-2382
Kulibekov, M. R., see Shostakovskii, M. F.-563
Kulibekov, M. R., see Shostakovskii, M. F.-926
Kulibekov, M. R., see Shostakovskii, M. F.-1588
Kulibekov, M. R., see Shostakovskii, M. F.-2376
Kulibekov, M. R., see Shostakovskii, M. F.-2862
Kulibekov, M. R., see Shostakovskii, M. F.-2864
Kuliulin, I. P., see Gladshtein, B. M.-2454
Kul'kina, S. D., see Malenok, N. M.-421
Kul'kina, S. D., see Malenok, N. M.-427
Kupin, B. S., see Petrov, A. A.-2041
Kuranova, I. P., see Akimova, L. N.-391
Kurdiumova, K. N., see Braz, G. I.-3001
Kurdiumova, K. N., see Mikhailov, B. M.-352
Kurdiumova, T. N., see Dokunikhin, N. S.-2021
Kuriakova, L. G., see Shtifman, L. M.-2066
Kurkevichus, S. I., see Vorozhtsov, N. N., Jr.-2710
Kurliankina, V. I., see Koz'mina, O. P.-3230
Kursanov, D. N., see Parnes, Z. N.-402
Kursanov, D. N., see Vol'pin, M. E.-326
Kustol, D. M., see Karishin, A. P.-673
Kutepov, D. F., and A. A. Potashnik and D. N. Khokhlov. Synthesis of Diureines of Some Nitrophenanthrenequinones-663
Kutsenko, A. I., see Liubomilov, V. I.-1928
Kuz'mina, Iu. L., see Spryskov, A. A.-185
Kuznetsov, S. G., and Z. I. Bobysheva. Synthesis of Some Aminoalkyl Ethers with Cholinolytic Properties-511
Kuznetsov, S. G., Z. I. Bobysheva and E. M. Balonova. Synthesis of Tagged Diethylaminoethyl S^{35}-Diphenylhydroxythioacetate-618

Kuznetsov, S. G., and V. N. Nikitin. Investigation of the Hydrogen Bond in Some Cholinolytic Substance Using Infrared Absorption Spectra-515
Kuznetsova, E. M., see Perveev, F. Ia.-2397
Kuznetsova, N. A., see Sarycheva, I. I.-630
Kuzovkov, A. D., Investigation of Aconite Alkaloids. XI. Oxidation of the Hydrocarbon $C_{18}H_{18}$, Formed During Dehydrogenation of Songorine -549
Kuzovkov, A. D. A Study of Aconite Alkaloids. XII. Structure of the Hydrocarbon $C_{18}H_{18}$ and the Possible Formula of Songorine-2320
Kuzovkov, A. D., and A. V. Bocharnikova. Investigation of Aconite Alkaloids. X. Elatine. Structure of Esterifying Acid-547
Kuzovkov, A. D., see Platonova, T. F.-259
Kuzovkov, A. D., see Platonova, T. F.-3157
Kuzovkov, A. D., see Platonova, T. F.-3159
Kuzovkov, A. D., see Platonova, T. F.-3162
Kviat, E. I. Dissociation of Arylcarbinols and Some Other Compounds In Nitrobenzene. II-2296
Kviat, E. I., and Ginzburg, O. F. The Problem of the Dissociation of Arylcarbinols and Some Other Compounds in Nitrobenzene-52

Labenskii. A. S. Investigation of the Crystalline Substance Formed in the Production of Anabasine Sulfate-537
Labenskii, A. S., I. I. Gerasimenko and L. M. Utkin. The Glycosidic Alkaloid of the Plant *Solanum Mergaparcum* Koidz. (Large-Fruited Nightshade)-3150
Labenskii, A. S., see Matsova, L. G.-2631
Labynskii, I. P. Condensation of Diacetone Alcohol with Benzene-1676
Lagidze, V. F., see Stepanov, B. I.-1956
Lamiaeva, V. N., see Razuvaev, G. A.-2270
Lapinskaia, E. M., see Khenokh, M. A.-658
Lapinskaia, E. M., see Khenokh, M. A.-679
Lapkin, I. I., and Belonovich, M. Reactions of Halometal Alcoholates. VI. A New Method of Synthesis of Monohydroxytriarylmethanes-586
Lapkin, I. I., O. M. Lapkina and M. N. Rybakova. Reactions of Metal Alcoholate Halides. V. The Mechanism of the Reaction of Magnesium Carbinolate Halides with Ester-385
Lapkin, I. I., and O. M. Lapkina. Steric Hindrance in Organomagnesium Reactions. XIX. Synthesis of Esters of α-(4-Alkoxy-1-naphthyl)Lactic Acid-933
Lapkin, I. I., and V. Ia. Vlasova. Steric Hindrance in Organomagnesium Reactions. XVIII. Synthesis of Esters of α-(β-Alkoxy-1-naphthyl)Lactic Acids-930
Lapkina, O. M., see Lapkin, I. I.-385
Lapkina, O. M., see Lapkin, I. I.-933
Lavrenova, G. I., see Poddubnaia, N. A.-396
Lavrova, L. V., see Evstigneeva, R. P.-1246
Lazarev, A. N., see Voronkov, M. G.-2167
Lebedev, N. N. The Mechanism of the Catalytic Action of Aluminum Chloride. VI. More About the Kinetics and Mechanism of the Alkylation of Benzene with Chloro Derivatives-1211
Lebedev, O. V., see Khmel'nitskii, L. I.-2340
Lebedev, O. V., see Novikov, S. S.-2333
Lebedev, O. V., see Novikov, S. S.-2342
Lebedeva, A. I., and L. F. Almashi. Investigation of Isomerization and Dimerization of Dimethylvinylcarbinol Relative to the pH of the Reagent. III. The Effect on Dimethylvinylcarbinol of Hydrochloric Acid, Saturated with Sodium and Magnesium Chlorides, and Hydrofluoric Acid-876
Lebedeva, A. I., and L. V. Kukhareva. Study of the Isomerization and Dimerization of Dimethylvinylcarbinol as a Function of the pH of the Reagent-2806
Leets, K. V. A Study of Iono-Catalytic Telomerization. I. Telomerization of Isoprene with Its Hydrochloride-1868
Leets, K. V. Catalytic Ionic Telomerization. II. The Composition of the Fraction of Terpene Chlorides in the Product of Telomerization of Isoprene with Its Hydrochlorides. Linalyl Chloride-3127
Leporskaia, E. A., and A. A. Petrov. Conjugated Systems. LXXXVIII. Condensation of 3-hexadiene with Propargylaldehyde and Propiolic Acid-1486
Lerman, Z. A., see Kh. V. Bal'ian-110
Lerner, O. M., see Perekalin, V. V.-1861
Letina, Z. I., see Egorov, Iu. P.-3284
Letina, Z. I., see Petrov, A. D.-589
Levchenko, E. S., see Kirsanov, A. V.-1639
Levchenko, N. F., see Litvinenko, L. M.-2086
Levin, B. B., see Bruker, A. B.-2752
Levina, L. I., S. N. Patrakova and D. A. Patrushev. Dependence of the Yield and the Quality of Benzenesulfonyl Chloride on the Excess of Chlorosulfonic Acid and Addition of Sodium Salts-2464
Levina, R. Ia., P. A. Kaikaris, A. V. Simolin and E. G. Treshchova. Synthesis of Hydrocarbons. LXVI. C_{11}-C_{16} Hydrocarbons with Two Adjacent Quaternary Carbon Atoms-2347
Levina, R. Ia., P. A. Kaikaris and P. A. Gembitskii. Synthesis of Hydrocarbons. LXVII. C_{12} Hydrocarbons with One and Two Quaternary Carbon Atoms-2849
Levina, R. Ia., V. N. Kostin. Interaction of Cyclopropane Hydrocarbons with Mercuric Salts. VIII. Reaction of γ-Mercurated Alcohols with Zinc Dust-3332

Levina, R. Ia., Iu. S. Shabarov and V. K. Daukshas. The Synthesis of Hydrocarbons. LXV. Di-tert-alkylmethanes from 2,4-Dimethyl-1,3-pentadiene-2089
Levina, R. Ia., see Lur'e, M. Iu.-1410
Levitskaia, K. V., see Danilov, S. N.-2978
Levshina, K. V., see Sergievskaia, S. I.-1884
Levshina, K. V., see Sergievskaia, S. I.-1890
Levshuk, M. Ia., see Andrianov, K. A.-330
Linevich, L. I. Synthesis of Alkoxy-Substituted Ketones of the Isoquinoline Series-1045
Linevich, L. I. Studies in the Field of Isoquinolinecarboxylic Acids. 2. Preparation of 7,8-Dimethoxyisocarbostyryl-3-carboxylic Acid, Its Esters and 7,8-Dimethoxyisocarbostyryl-2547
Linevich, L. I. Studies in the Field of Isoquinolinecarboxylic Acids. II. Preparation of 1-Chloro Substituted Carboxylic Acid of the Isoquinoline Series, Its Chloride and Esters and Some Data on Mobility of Chlorine in 1-Position of the Isoquinoline Nucleus-2551
Lishenkova, N. S., see Tishchenko, V. V.-1999
Lishnevskaia, L. A., see Zavel'skii, D. Z.-726
Lishnevskaia, L. A., see Zavel'skii, D. Z.-735
Lishnevskaia, L. A., see Zavel'skii, D. Z.-983
Lishnevskaia, L. A., see Zavel'skii, D. Z.-1966
Lishnevskaia, L. A., see Zavel'skii, D. Z.-2594
Lishnevskaia, L. A., see Zavel'skii, D. Z.-2602
Litvinenko, L. M., N. F. Levchenko and A. N. Androsov. The Synthesis of Some Nitro- and Amino Derivatives of Tolan-2086
Liubomilov, V. I. Reaction of Butyraldehyde with a Solution of Sodium Butoxide in n-Butanol-324
Liubomilov, V. I., and E. T. Belianina. On the Products Formed in the Condensation of n-Butanol in the Presence of Sodium Butoxide and a Copper Catalyst-322
Liubomilov, V. I., and A. I. Kutsenko. Intermediate Products in the Condensation Reaction of Isoamyl Alcohol-1928
Lobanova, E. F., see Bankovskii, Iu. A.-2884
Lomakina, V. I., see Mel'nikov, N. N.-466
Lopatenok, A. A., see Danilov, S. N.-3213
Lopatenok, A. A., see Danilov, S. N.-3218
Lopatin, B. V., see Nazarov, I. N.-1195
Losev, I. P., and O. V. Smirnova. Reaction of Aromatic Compounds with Alcohols in the Presence of Acid Catalysts. III. Reaction of Phenol with Diols in the Presence of Phosphoric Acid-359
Losev, I. P., and O. V. Smirnova. Reaction of Aromatic Compounds with Alcohols in the Presence of Acid Catalysts. IV. Reaction of Benzene with Polyhydric Alcohols in the Presence of Acid Catalysts-965
Losev, I. P., and O. V. Smirnova. Reaction of Aromatic Compounds with Alcohols in the Presence of Acid Catalysts. V. Reaction of Benzene with Polyvinyl Alcohol in the Presence of Acid Catalysts-968
Lugovkin, B. P. Condensation of 6-Quinolinealdehyde with Ketones and Esters-980
Luksha, E. A., see Bankovskii, Iu. A.-2310
Luneva, L. K., see Sladkov, A. M.-2921
Lur'e, M. Iu., I. S. Trubnikov, N. P. Shusherina and R. Ia. Levina. δ-Lactones. XII. Synthesis and Properties of 6-Phenyl-3,4-Dihydro-α-Pyrone-1410
Lur'i, F. A., see Maksimov, V. I.-2910
Lur'i, F. A., see Maksimov, V. I.-2913
Lutkova, V. I., and B. B. Berezina. Synthesis of Some Bifunctional Compounds Containing Sulfidic Sulfur-1320
Lutskii, A. E., E. M. Obukhova and I. A. Sidorov. Properties of Binary Mixtures of Organic Compounds as a Function of Association and Concentration-2423
Lysenko, Iu. A., and O. A. Osipov. Studies of the Reactions of Titanium Tetrachloride with Esters of Monobasic Acids. XII. The Decomposition of the Compounds $TiCl_4 \cdot$Ester-1771

Machinskaia, I. V., and V. A. Barkhash. On Some Properties of Enol Acetates. III. Preparation of Furan and Pyran Derivatives from Bromo-Substituted Enol Acetates-2899
Machinskaia, I. V., and A. S. Podberezina. The Problem of the Bromination of Cyclic Ketones with Dioxane Dibromide-1550
Madaeva, O. S. Steroid Sapogenins. III. The Sapogenins of the Rhizomes and Leaves of Yucca Filamentosa from the Black-Sea Coast of Caucasia-541
Madaeva, O. S. Steroidal Sapogenins. IV. A New Saraponine Isolated from Roots of Yucca Filamentosa-2029
Madaeva, O. S., see Serova, N. A.-2032
Mai, L. A. Relation Between the Acidity of Acyclic Polyols and the Length of the Polyhydroxylmethylene Chain-1304
Mai, L. A. The Acidity of Some Monosubstituted Acetic Acids and the Electronic Affinity of Substituents-1306
Mai, L. A., The Number of Optical Stereoisomers and Their Distribution with Respect to the Different Types of Configuration in Compounds with Continuous Series of Asymmetric Centers in an Unbranched Chain-2887
Maimind, V. I., O. M. Enisherlova, K. M. Ermolaev, R. G. Vdovina, G. A. Galegov and M. M. Shemiakin. Investigation in the Field of

Compounds Labeled with C^{14} and N^{15}. IX. Synthesis of ω-N^{15}-Amino Acids-2260
Maimind, V. I., see Shemiakin, M. M.-952
Maimind, V. I., see Shemiakin, M. M.-1756
Makalets, B. I., see Verezin, I. V.-2746
Makarov, N. V., see Iur'ev, Iu. K.-857
Makarov, S. P., see Iakubovich, A. A.-1006
Makarova, A. N., see Mikhailov, B. M.-149
Makhmutova, F. I., see Abramov, V. S.-647
Makitra, R. G., see Kirsanov, A. V.-35
Makitra, R. G., see Kirsanov, A. V.-1283
Makliaev, F. M., see Titov, A. I.-551
Maksimov, V. I., and G. S. Grinenko. Investigation in the Field of the Synthesis of Steroid Hormone Analogs. V. The Synthesis of Some Compounds of the Cyclopentanotetrahydronaphthalene Series-2218
Maksimov, V. I., and G. S. Grinenko. Investigation in the Field of the Synthesis of Steroid Hormone Analogs. VI. Experiments on the Cyclization of Trans-3-(p-methoxyphenyl)-cyclopentano-1-one-2-acetic Acid and Its Derivatives-2222
Maksimov, V. I., F. A. Lur'i and G. P. Krupina. The Preparation of Δ^{23}-3-Keto-24,24-diphenylcholene-2910
Maksimov, V. I., F. A. Lur'i and G. F. Krupina. The Preparation of Pregnane-3,20-dione from Δ^{23}-3-Keto-24,24-diphenylcholene-3-ethylene Ketal-2913
Maksimov, V. I., and Z. A. Priakhina. Analogs of Steroid Hormones. I. Preparation of 3-(4-Oxocyclohexyl)-2-Methylcyclopentanol-247
Maksimov, V. I., and Z. A. Priakhina. Analogs of Steroid Hormones. II. Synthesis of 6-(2-Methyl-3-Hydroxypentyl)-$\Delta^{1(9)}$ Octalone-253
Maksimov, V. I., see Grinenko, G. S.-519
Maksimov, V. I., see Grinenko, G. S.-522
Maksiutina, N. P. Cardiac Glycosides of the Seeds of Worm-Seed Mustard (*Erysimum cheiranthoides* L.)-1441
Malenok, N. M., S. D. Kul'kina and Z. Iu. Kotunenko. Oxidation of Vinylacetylenic Hydrocarbons by Organic Hydroperoxides. V. Oxidation of 6,9-Dimethyl-5,9-Tetradecadien-7-yne, 4,7-Dimethyl-3,7-Decadien-5-yne and 3,6-Diethyl-2,6-Octadien-4-yne by Acetyl Hydroperoxide-421
Malenok, N. M., and S. D. Kul'kina. Oxidation of Vinylacetylenic Hydrocarbons by Organic Hydroperoxides. VI. Oxidation of 1-Phenyl-3-Methylocten-3-yne-1 by Acetyl Hydroperoxide-427
Malevannaia, Z. P., see Fol'mov, V. P.-3106
Malinovskii, M. G., see Gitis, S. S.-2299
Maliugina, N. I., see Vertiulina, L. N.-301
Mamedov, Shamkhal, and A. F. Aliev. Ethers of Glycols and Their Derivatives. XXXII. Synthesis of Monoethers of γ-Glycols and Their Alkoxymethyl Derivatives-897
Mamedov, Shamkhal and B. Pishnamazzade. Studies in the Field of Glycol Ethers and Their Derivatives. XXXIV. Chemical Transformations of γ-Chloroethers-1879
Mamedov, Shamkhal and B. K. Zeinalov. Studies in the Field of Glycol Ethers and Their Derivatives. XXXIII. Some Chemical Transformations of γ-Bromoethers of the Aliphatic Series-1876
Mandel'baum, Ia. A., N. N. Mel'nikov and N. I. Petrova. Organic Insectofungicides. XXXII. Synthesis of Some Mixed Esters of Thiophosphoric Acid-469
Mandel'baum, Ia. A., see Mel'nikov, N. N.-466
Mandel'baum, Ia. A., see Mel'nikov, N. N.-2507
Maretina, I. A., see Aizikovich, M. A.-3076
Markova, Iu. V., L. N. Zenkova and M. N. Shchukina. The Synthesis of Mercaptoamino Compounds. III. Synthesis of 3-Mercapto-4-amino-2-methylbutane and 5-Amino-1-mercaptopentane-1856
Markovich, E. A., see Razumov, A. I.-194
Martynov, V. F., and Kastron, Ia. A. Studies in the Field of Compounds which Contain Three-Membered Oxygen Rings. XXIII. The Reaction of Ethyl Esters of β-Methyl-β-butyl and β-Methyl-β-phenylglycidic Acids with Aniline-2119
Martynov, V. F., and G. Ol'man. Investigation of Compounds Containing a Three-Membered Oxide Ring. XX. Reaction of Ethyl Esters of β-Nitrophenylglycidic Acids and p-Chlorophenylglycidic Acid with Ammonia and Aniline-576
Martynov, V. F., and A. V. Shchelkunov. Investigation in the Field of Compounds Containing a Three-Membered Oxide Ring. XXIV. Synthesis of β,β'-Disubstituted Nitriles of Glycidic Acids-3275
Martynov, V. F., and Sukhinin, N. P. Studies in the Field of Compounds which Contain Three-Membered Oxide Rings. XXII. The Reaction of Glycidic Acid Esters with α- and β-Naphthylamines-2113
Martynov, V. F., and Vasiutina, Zh. D. Investigation of Compounds Containing a Three-Membered Oxide Ring. XXI. Reaction of Amides of β-Tetra- and β-Pentamethyleneglycidic Acids with Hexyl- and Benzylamines-583
Maslennikova, V. A., see Abubakirov, N. K.-2316
Maslennikova, V. A., see Sultanov, A. S.-765
Maslianskii, G. N., and Bursian, N. R. Dehydrogenation Kinetics of Cyclohexane and Its Homologs on a Chromium Catalyst at Atmospheric Pressure-2684

Maslianskii, G. N., and Bursian, N. R. A Study of the Dehydrogenation of Cyclohexane on a Chromium Catalyst Under a Pressure of Hydrogen-2690
Maslov, P. G., and Klochikhin, A. A. The Molecular Refraction of Certain Classes of Alkylthiophenes and Alkylthiacycloalkanes-811
Massagetov, P. S., see Platonova, T. F.-259
Massagetov, P. S., see Platonova, T. F.-3157
Massagetov, P. S., see Platonova, T. F.-3159
Massagetov, P. S., see Platonova, T. F.-3162
Mastriukova, T. A., V. N. Odnoralova and M. I. Kabachnik. Reaction of Dialkyl Dithiophosphates with Ethylene Sulfide-1613
Matiukhina, L. G., see Riabinin, A. A.-2628
Matskanova, M. A., and Vanag, G. Ia. 1-Aminomethyl-4-phthalazone-2822
Matskevich, R. M., see Krasovitskii, B. M.-2520
Matsolan, S. G., see Nazarov, I. N.-2781
Matsova, L. G., and A. S. Labenskii. The Condensation Products of L-Ephedrine and D-Pseudoephedrine with Acetone-2631
Matveenko, L. I., see Kirsanov, A. V.-1935
Matveeva-Kudasheva, A. N., see Bobrova, M. I.-2958
Matveeva-Kudasheva, A. N., see Bobrova, M. I.-3323
Matveeva, E. N., see Koz'mina, O. P.-3230
Maurit, M. E., and N. A. Preobrazhenskii. Synthesis of N-Methyl-3-carbomethoxy-4-hydroxypiperidines and a Study of Their Steric Structures-943
Mavrov, M. V., see Nazarov, I. N.-3092
Mazurek, V. V., see Dolgov, B. N.-2433
Mel'kanovitskaia, S. G., and I. P. Tsukervanik. Radical and Ion Alkylation of the Aromatic Ring. VI. Reactions of Diphenylchloromethane with Toluene and Benzene-10
Mel'kanovitskaia, S. G., and I. P. Tsukervanik. Radical and Ionic Alkylation of the Aromatic Ring. VII. Butylation of Benzene, Naphthalene, Phenol and Anisole-2071
Mel'nikov, N. N., Ia. A. Mandel'baum and V. I. Lomakina. Organic Insectofungicides. XXXI. A New Method of Preparing Mixed Esters of Thiophosphoric Acid-466
Mel'nikov, N. N., Ia. A. Mandel'baum and Z. M. Bakanova. From the Field of Organic Insectofungicides. XXXIV. New Method of Synthesis of Trialkyl Phosphites-2507
Mel'nikov, N. N., and K. D. Shvesova-Shilovskaia. Organic Insectofungicides. XXX. Synthesis of Some Derivatives of 1-Methylcyclopentanedione-2,3-464
Mel'nikov, N. N., and S. D. Volodkovich. From the Fields of Organic Insectofungicides. XXXVI. On the Reaction of Tetrachloro- and Pentachlorocyclopentadienes with Certain Unsaturated Compounds-3342
Mel'nikov, N. N., see Kukalenko, S, S.-153
Mel'nikov, N. N., see Kukalenko, S. S.-471
Mel'nikov, N. N., see Mandel'baum, Ia. A.-469
Men'shikov, G. P., see Denisova, S. I.-1925
Merkur'eva, L. A., see Bal'ian, Kh. V.-110
Meshcheriakov, A. P., L. V. Petrova and Iu. P. Egorov. The Reactivity of α,β-Unsaturated Ketones and β-Ketone Halides in the Kizhner Reaction-2621
Mezentsova, N. N., see Iur'ev, Iu. K.-3071
Mezentsova, N. N., see Iur'ev, Iu. K.-3288
Mikhailov, B. M., and K. N. Kurdiumova. Structure and Chemical Transformations of Alkali-organic Compounds of Anils. III. Transformations of Disodium and Dilithium Compounds of Benzophenone-o-Tolylimide and Benzophenone-p-Tolylimide Under the Influence of Alkyl Halides-352
Mikhailov, B. M., and Makarova, A. N. Condensation of ω-Bromoacetophenone with Diethanolamine-149
Mikhailova, V. N., and Pigulevskii, V. V. Addition of Hydrogen Halides to Esters of α,β-Unsaturated Acids-2302
Mikhailova,V. N.,and V. V. Pigulevskii. Synthesis of 1-Phenyl-3-pyrazolidone (Phenidone) from Esters of β-Chloropropionic Acid-3142
Mikhant'ev, V. I., and L. P. Pavlov. Vinylation of Hydrobenzoin. I-478
Mikheeva, N. N., see Nazarov, I. N.-936
Mikheeva, N. N., see Nazarov, I. N.-2469
Mikheeva, N. N., see Nazarov, I. N.-2771
Mikhlina, E. E., and M. V. Rubtsov. Synthesis of Quinuclidine-3-Acetic Acid-104
Mikhlina, E. E., and M. V. Rubtsov. Synthesis of 6,7-Disubstituted Derivatives of 1-Azobicyclo-(3,2,1)-Octane-1228
Mikhlina, E. E., see Furshtatova, V. Ia.-650
Mikhlina, E. E., see Nikitskaia, E. S.-2810
Miklashevskaia, V. S., and Petrov, A. A. Studies in the Field of Conjugated Systems. LXXXV. The Condensation of Diene Halides with Acetylene Dicarboxylic Ester-1187
Mingaleva, K. S., see Petrov, A. A.-2357
Minkin, V. I., and Ardashev, B. I. A New Method for the Preparation of Quinaldine Bases and N-Arylquinaldinium Salts by the Condensation of Arylamines with Aldehydes. XX-2590
Minkin, V. I., see Ardashev, B. I.-535
Minkin, V. I., see Ardashev, B. I.-1627
Minsker, K. S., see Razuvaev, G. A.-957
Mishina, V. G., see Terent'ev, A. P.-222
Mishina, V. G., see Terent'ev, A. P.-1566
Miskidzh'ian, S. P. Electrolytic Dissociation in

Nonaqueous Systems. VI. System Allyl Mustard Oil–o-Toluidine-278
Mitin, Iu. V. Preparation of Certain Compounds with Two Isopropenyl Groups-3328
Mkrian, G. M., see Babaian, A. T.-1314
Mukhacheva, O. A., see Razumov, A. I.-194
Muler, L. I., see Iakubovich, A. Ia.-313
Mur, V. I. Internal Complex Salts of Azo Compounds. V. Coppering of o-Hydroxy-o'-Alkoxyazo Compounds with Simultaneous Dealkylation-972
Mushkalo, L. K. The Condensation of o-Aminothiophenols with Unsaturated Ketones and β-Haloketones-498
Mushkalo, L. K. Condensation of o-Aminothiophenols with β-Haloketones. Synthesis of Quaternary Salts in the Dihydrobenzohepta-1,5-Thiazine Series III-723
Myshliaeva, L. V., see Kreshkov, A. P.-2150
Moglianskii, Ia. D., see Terent'ev, A. P.-2002
Molosnova, V. P., see Kirsanov, A. V.-31
Molosnova, V. P., see Kirsanov, A. V.-344
Morozova, E. A., and S. M. Zhenodarova. The Formation of 5-Benzylhydantoin-3-acetylvaline from the Methyl Ester of N-Carbobenzoxyphenylalanylglycylvaline-1708
Morozova, E. A., and S. M. Zhenodarova. The Synthesis of Cyanomethyl Esters of Peptides and Their Use in Obtaining Peptides-1711
Morozova, M. P., see Ariia, S. M.-2647
Morozova, M. P., see Shchukarev, S. A.-3315
Morozovskaia, L. M., see Suvorov, N. N.-2634
Morozovskaia, L. M., see Suvorov, N. N.-1433
Mosichkin, Iu. M., see Ponomarev, F. G.-2293
Motornyi, S. P., see Iarovenko, N. N.-2541
Motovilova, N. N., see Iakubchik, A. I.-413
Motsarev, G. V., A. L. Englin, A. Ia. Iakubovich, I. N. Uspenskaia and N. G. Ivanova. On the Liquid-Phase Catalytic Chlorination of Methylchlorosilanes-1395
Motsarev, G. V., and Iakubovich, A. Ia. Halogenation of Aromatic Silanes. VI. Preparation and Properties of Chloro Derivatives of p-(Trichloromethyl)-phenyltrichlorosilane-2754
Mozgova, K. K., see Korshak, V. V.-2874

Naidenova, I. N., see Pigulevskii, G. V.-234
Naryshkina, T. I., see Kukalenko, S. S.-471
Naumova, S. F., see Emel'ianov, N. P.-1342
Nazarov, I. N., and Akhrem, A. A. The Simplest Analogs of Corticosteroids. II. Introduction of Dihydroxycarboxylic, Glycerol and Hydroxylacetone Side Chains into o-Methylcyclohexanone and the Stereochemistry of the Compounds Formed Thereby-1838
Nazarov, I. N., Akhrem, A. A., and A. V. Kamernitskii. A Study in the Field of Stereochemistry of Cyclic Compounds. 28. Steric Directivity of the Serini Reaction in the Cyclohexane Series-1850
Nazarov, I. N., G. V. Aleksandrova and A. A. Akhrem. The Simplest Analogs of Corticosteroids. III. The Introduction of Dihydroxyacetone, Glycerol and Dihydroxypropanecarboxylic Acid Side Chains into Derivatives of Cis- and Trans-Decalins-2227
Nazarov, I. N., G. V. Aleksandrova and A. A. Akhrem. Synthesis and Transformations of Cis- and Trans-1-ethynyl-1-decalols-2237
Nazarov, I. N., L. D. Bergelson, L. P. Badenkova and B. V. Lopatin. Acetylene Derivatives. 192. The Stereochemistry of Hydrogenation of Acetylenic Glycols-1195
Nazarov, I. N., and Cherkasova, E. M. Synthetic Anesthetics. XXII. Phenoxyacetates of 1-Phenyl-3-dimethylaminopropane-1-ols-122
Nazarov, I. N., E. M. Cherkasova and Ch'ang Ch'ung-kwang. Synthetic Anesthetics. XXIII. Phenoxyacetates of 1-Phenyl-2-methyl-3-dialkylaminopropan-1-ols-127
Nazarov, I. N., E. M. Cherkasova and Ch'ang Ch'ung-kwang. Synthetic Analgesics. XXIV. Esters of 1-Phenyl-2,2-dimethyl-3-dialkylaminopropan-1-ols-443
Nazarov, I. N., B. P. Gusev and V. I. Gunar. Acetylene Derivatives. 193. Total Synthesis Isoprenoid Alcohols (Linalool, Geraniol, Nerol, Nerolidol, Farnesol, Geranyllinalool, Geranyl-Geraniol and Phytol)-1498
Nazarov, I. N., A. V. Kamernitskii and A. A. Akhrem. Simpler Analogs for Corticosteroids. I. Stereochemistry of Cyanohydrin and Acetylenic Synthesis. Configuration of 1-Cyano- and 1-Ethynyl-2-methylcyclo-hexanols-1511
Nazarov, I. N., and Zh. A. Krasnaia. Condensation of Acetals with 1-Ethoxydienes. A New Method of Synthesis of Polyene Aldehydes of Isoprene Type-2477
Nazarov, I. N., Zh. A. Krasnaia and V. P. Vinogradov. Acetylene Derivatives. 190. Preparation of Ethoxyacetylene and Its Employment for the Synthesis of Unsaturated Aldehydes and Acids-451
Nazarov, I. N., and M. V. Mavrov. Diene Condensations of Gem-Substituted Butadienes. I-3092
Nazarov, I. N., N. S. Prostakov, and N. N. Mikheeva. Heterocyclic Compounds. 61. Synthetic Analgesic Substances. XXV. Esters of 1,2,5-Trimethyl-4-phenyl(aryl)-4-piperidol-936
Nazarov, I. N., N. S. Prostakov and N. N. Mikheeva. Heterocyclic Compounds. LXII. Stereochemistry of 1-Acyl-2,5-Dimethyl-4-piperidones-2469

Nazarov, I. N., N. S. Prostakov and N. N. Mikheeva. Heterocyclic Compounds. 63. Synthetic Analgesics. XXVI. Stereoisomerism of 2,5-Dimethyl-4-piperidols and 1-Acyl-2,5-dimethyl-4-phenyl-4-piperidols-2771

Nazarov, I. N., S. A. Vartanian and S. G. Matsolan. Acetylene Derivatives. CXCIV. Hydration of Divinylacetylene and Vinylisopropenylacetylene in Alcohol Solutions-2781

Nazarova, L. M. A Study of the Mobility of the Ethyl Group in Ethylbenzene and Its Derivatives by the Method of Isotope Exchange-2082

Nazarova, Z. N., and F. T. Pozharskii. 5-Chlorofurylnitroolefins-1553

Nechaeva, O. N., and Z. V. Pushkareva. Investigation of Heterocyclic N-Oxides. VI. Polarographic Reduction of Some N-Oxides of Phenazines and Acridines-2721

Nechaeva, O. N., see Pushkareva, Z. V.-2729

Neiland, O. Ia., G. Ia. Vanag and E. Iu. Gudrinietse. Iodonium Derivatives of β-Diketones. II. Thermal Decomposition of Phenyldimedonyliodone-1256

Nekrasova, V. A., The Chlorination of n-Hexane and n-Heptane-1606

Nekrasova, V. A. The Problem of the Production of Aliphatic Alcohols from Petroleum Hydrocarbons-1610

Nekrasova, V. A., N. I. Shuikin and S. S. Novikov. Chlorination of Five- and Six-membered Cyclanes. -15

Nekrasova, Z. D., see Kirsanov, A. V.-1644

Nemodruk, A. A. The Action of Nitrous Acid on Cyclic Salts of Salicylic Acid. The Preparation of 5-Diazosalicylic Acid-1051

Nemodruk, A. A. The Preparation of o-Nitrosophenol from Salicylic Acid-2701

Nesterenko, L. T., see Rozina, D. Sh.-2904

Neterman, V. A., see Shostakovskii, N. F.-2866

Nikiforova, O. K., and N. N. Suvorov. Steroids. I. Preparation of 21-Bromopregnanol-17α-Trione-3,11,20 from Pregnanol-3β-dione-11,20-2025

Nikolenko, L. N., and K. K. Babievskii. Investigation of Aromatic Compounds with a Long Side Chain. II. Preparation of Dodecylaniline by Ammonolysis of p-Chlorododecylbenzene-238

Nikishin, G. I., see Petrov, A. D.-1809

Nikishin, G. I., see Petrov, A. D.-2122

Nikishin, G. I., see Petrov, A. D.-2353

Nikitin, V. N., see Kuznetsov, S. G.-515

Nikitskaia, E. S., E. E. Mikhlina, L. N. Iakhontov and V. Ia. Furshtatova. Synthesis of Hydrazides and Hydrazones of Some Heterocylic and Aromatic Acids-2810

Nikitskaia, E. S., V. S. Usovskaia and M. V. Rubtsov. Tertiary Amines of Some Heterocyclics as Possible Hypotension Remedies-161

Nikolaevich, Stepan. High Esteemed and Dear-3189

Nirenburg, V. L., I. Ia. Postovskii and V. M. Cherkasov. Some Aryl Derivatives of Cyanothiourea-198

Nogaideli, A. I., K. Ia. Dzagnidze and R. Papava. Synthesis of 6-Methyloctene-1-yne-4-diol-3,6- and 7-Methyloctene-2-yne-5-diol-4,7 and Their Catalytic Hydrogenation-116

Nogaideli, A. I., and Gonadze, G. M. Synthesis of Acetic Ester of Bis(Hydroxycyclohexyl)-1,3-Butadiyne and Its Catalytic Hydrogenation-895

Novikov, G. I., see Shchukarev, S. A.-2040

Novikov, S. S., L. I. Khmel'nitskii and O. V. Lebedev. Reaction of Nitrogen Tetroxide with Organic Compounds. I. A Study of Conditions of Reaction of Nitrogen Tetroxide with Benzaldoxime. Composition of Products and Reaction Equation-2333

Novikov, S. S., O. V. Lebedev, L. I. Khmel'nitskii and Iu. P. Egorov. Reaction of Nitrogen Tetroxide with Organic Compounds. III. Reaction of Nitrogen Tetroxide with Salts of Aliphatic Nitro Compounds-2342

Novikov, S. S., see Khmel'nitskii, L. I.-2340

Novikov, S. S., see Nekrasova, V. A.-15

Novikova, E. N. Effect of Substituents in the Molecules of Inhibitors on Their Protective Properties in Autoxidation of α-Pinene-2035

Novoselova, E. K., see E. G. Berdichevskii-670

Novotorov, N. E., see Korshunov, I. A.-48

Obukhova, E. M., see Lutskii, A. E.-2423

Odnoralova, V. N., see Mastriukova, T. A.-1613

Ogloblin, K. A. The Reaction of Nitrosyl Chloride with Unsaturated Hydrocarbons. IV. The Reaction with Butene-1-3272

Okun', M. G., see Danilov, S. N.-3221

Okun', M. G., see Plisko, E. A.-3203

Ol'dekop, Iu. A., and T. V. Vasilevskaia. Reaction of Mercuric Pivalate with Peroxides, and with Light-3037

Ol'man, G., see V. F. Martynov-576

Omel'chenko, S. I., and Z. V. Pushkareva. Investigation of Structural Features and Chemical Conversions of Carbazole and Some of Its Derivatives. II. Some Properties of 3- Aminocarbazole and Its Derivatives-2733

Opanasenko, E. P., see Piliugin, G. T.-1374

Orekhova, K. M., see Kukhtin, V. A.-2814

Orlova, A. A., see Korshunov-45

Ormont, B. F., and E. I. Smagina. Enthalpy of Formation of Nickel Carbonyl-281

Oshkaia, V. O., see Vanag, G. Ia.-1570
Oshueva, N. A., see Temnikova, T. I.-3252
Osipenko, I. F., see Pansevich-Koliada, V. I.-624
Osipenko, I. F., see Pansevich-Koliada, V. I.-881
Osipov, O. A., see Lysenko, Iu. A.-1771
Ovsiannikova, L. A., see Sokolova, T. A.-757
Ozol, Ia. K., V. N. Zelmen and G. Ia. Vanag. 2-Diphenylacetyl-1,3-Indanedione-3114

Paikn, D. M., see Kabachnik, M. I.-1618
Paiadienko, N. P., see Plisov, A. K.-494
Pal'gi, M. Synthesis of Some Isomeric Methoxy-Allyl Diethylaminoethoxybenzenes-2275
Panifilov, G. A., see Bedniagina, N. P.-361
Panova, N. I., see Kozlov, N. S.-2421
Pansevich-Koliada, V. I. 1-Phenyl-3-Bromobutene-2 in the Grignard Reaction-430
Pansevich-Koliada, V. I., and Z. B. Idel'chik. Investigation of Oxido Compounds. XI. Reaction of α-Oxides of Allyl Ethers of Phenol, p-Cresol and Guaiacol with Methyl Aclohol-887
Pansevich-Koliada and I. F. Osipenko. Investigation of Ethers with a Double Bond in the Allyl Position II. Synthesis of Ethers of α,α,γ,γ-Tetraalkyl-Substituted Allyl Alcohols-624
Pansevich-Koliada, V. I., and I. F. Osipenko. Investigation of Ethers with a Double Bond in the Allyl Position. III. Study of the Etherification of α,α-γ,γ-Tetraalkyl Substituted Allyl Alcohols-881
Pansevich-Koliada, V. I., see Idel'chik, Z. B.-770
Papava, R., see Nogaideli, A. I.-116
Parnes, Z. N., S. V. Vitt and D. N. Kursanov. Investigation of Pinacoline Isomerization Using Labeled Atoms-402
Patrakova, S. N., see Levina, L. I.-2464
Patrina, N. D., see Reutov, O. A.-572
Patrushev, D. A., see Levina, L. I.-2464
Pavliuchenko, M. M., see Ermolenko, I. N.-704
Pavlov, L. P., see Mikhant'ev, B. I.-478
Pavlova, L. A., A. Fabritsy and E. D. Venus-Danilova. Investigation of the Conversion of Pinacols with Substituted Acetylene Radicals. XV. Action of Mercuric Sulfate on Unsym. Dimethylphenyl (Phenylethynyl)- and Usym. Methyldiphenyl (Phenylethynyl) Ethylene Glycols-634
Pechka, A. A., see Grigor'eva, N. E.-1726
Perekalin, V. V., and O. M. Lerner. The Reaction of Dinitrodiolefins with Compounds which Contain Mobile Hydrogen in Methylene Groups-1861
Perekalin, V. V., and A. S. Sopova. Synthesis of γ-Amino Ketones-656
Perveev, F. Ia., and E. M. Kuznetsova. Reaction of Ammonia and Amines with Oxides of Acetylenic and Vinylacetylenic Series. New Methods for the Preparation of Pyrrole Homologs-2397
Pesin, V. G., and A. M. Khaletskii. Studies in the Field of the Chemistry of 2,1,3-Thiodiazole. VI. Chlorination and Bromination of 4- and 5-Aminobenzo-2,1,3-Thiodiazoles-20
Pesin, V. G., and A. M. Khaletskii. Investigations in the Field of 2,1,3-Thiodiazole Chemistry. VII. Thiocyanation of 4- and 5-Aminobenz-2,1,3-Thiodiazoles-378
Pesin, V. G., A. M. Khaletskii and Chou Ch'in. Studies in the Field of the Chemistry of 2,1,3-Thiodiazole. VIII. The Oxidation of Benzo-2,1,3-Thiodiazole and Its Derivatives-2126
Pesin, V. G., A. M. Khaletskii and Chou Ch'in. Chemistry of 2,1,3-Thiadiazole. IX. Reaction of o-Benzoquinone Dioxime with Sulfur Dichloride-2131
Pesin, V. G., A. M. Khaletskii and Teng Jun-hsiang. Chemistry of Pyrazolidine. II. Halogenation and Thiocyanation of 1,2-Diphenyl-3,5-dioxopyrazolidine and Its Derivatives-2841
Pesin, V. G., A. M. Khaletskii and Teng Jun-hsiang. Chemistry of Pyrazolidine. IV. Synthesis and Study of Sulfides and Disulfides of 1,2-Diphenyl- and n-Butyl-1,2-diphenyl-3,5-dioxopyrazolidine-3060
Pesin, V. G., A. M. Khaletskii and Teng Jun-hsiang. Investigations in the Field of the Chemistry of Pyrazolidine. V. On Some Anomalous Reactions of 1,2-Diphenyl-3,5-dioxopyrazolidine and Its Halogen and Thiocyanogen Derivatives-3300
Pesin, V. G., see Khaletskii, A. M.-2386
Pesin, V. G., see Khaletskii, A. M.-2393
Pesin, V. G., see Khaletskii, A. M.-2845
Pesin, V. G., see Khaletskii, A. M.-3057
Petiunin, P. A., and L. A. Tetiueva. Reaction of Magnesylamines. V. The Mechanism of the Reactions of Aryl Amidation of Aromatic Aldehydes by N,N-bis-(halomagnesium)arylamines-1072
Petiunin, P. A., and L. A. Tetiueva. Reactions of Magnesylamines. VI. Steric Hindrance in the Aramidation of Aromatic Aldehydes with the Help of N,N'-bis-(halomagnesium)arylamines-1596
Petiunin, P. A., see Konshin, M. E.-949
Petiunin, P. A., see Tetiueva, L. A.-719
Petrashko, Iu., see Andrianov, K.-666
Petrov, A. A. Investigations in the Field of Conjugated Systems. LXXXIV. Dienyne Compounds. I. Synthesis and Properties of β-Alkoxydivinylacetylenes (Enol Ethers of Methylvinylethynyl Ketone)-621
Petrov, A. A., Kh. V. Bal'ian, Iu. I. Kheruze, E. Iu. Shvarts and L. I. Cherenkova. Conjugated Systems. LXXXIX. Influence of Various Factors on the Yield of Geranyl Chloride in the Reaction of Isoprene with Its Hydrochlorides-1490

Petrov, A. A., and B. S. Kupin. Concerning the Order of Addition of Water and Alcohols to Vinylalkylacetylenes-2041
Petrov, A. A., Iu. I. Porfir'eva, T. V. Iakovleva and K. S. Mingaleva. Investigations on Conjugated Systems. XCII. Sequence of Addition of Iodine to Vinylacetylenic Hydrocarbons-2357
Petrov, A. A., Iu. I. Porfir'eva, and G. I. Semenov. Investigations of Conjugated Systems. XCIII. The Sequence of Addition of Alkyl Hypobromites to Vinylalkylacetylenes-2362
Petrov, A. A., K. B. Rall and G. I. Semenov. Investigations on Conjugated Systems. LXXXIII. The Structure and Reactivity of the Methyl Ester of Vinylacetylene Carboxylic Acid-417
Petrov, A. A., N. A. Razumova and M. L. Genusov. Studies in the Field of Conjugated Systems. LXXXVI. The Combination of Piperylene Hydrochloride with Isoprene-1190
Petrov, A. A., N. A. Razumova and M. L. Genusov. Investigations in the Field of Conjugated Systems. XC. The Addition of 2-Chloro-3-pentene to Divinyl-2171
Petrov, A. A., and N. A. Razumova. Investigations in the Field of Conjugated Systems. XCI. The Addition of 1-Chloro-3-methyl-2-butene to Divinyl-2178
Petrov, A. A., N. A. Razumova and M. L. Genusov. Investigations in the Field of Conjugated Systems. XCV. Reactions of Piperylene with Its Hydrochloride and with the 1,4-Hydrochloride of Isoprene-3248
Petrov, A. A., and G. I. Semenov. Investigations on Conjugated Systems. LXXXII. Infrared Spectra of Vinylacetylenic and Dienic Ethers-73
Petrov, A. A., see Aizikovich, M. A.-3076
Petrov, A. A., see Aizikovich, M. A.-3082
Petrov, A. A., see Al'bitskaia, V. M.-873
Petrov, A. A., see Leporskaia, E. A.-1486
Petrov, A. A., see Miklashevskaia, V. S.-1187
Petrov, A. A., see Vovsi, B. A.-1481
Petrov, A. D., E. P. Kaplan, Z. I. Letina and Iu. P. Egorov. Metalloorganic Synthesis of Dibiphenylalkanes and Diphenylalkanes. III-589
Petrov, A. D., G. I. Nikishin and V. D. Vorob'ev. Synthesis of Undecyl and Dodecylbenzenes and Their Perhydrides-1809
Petrov, A. D., G. I. Nikishin and N. P. Smetankina. The Behavior of Some Dichloroalkanes and Dichloroalkenes in Conditions of Direct Synthesis-2122
Petrov, A. D., G. I. Nikishin, V. N. Gramenitskaia and V. D. Vorob'ev. Reaction of Tert-Butylbenzene β-(Magnesium Chloride) with Carbonyl Compounds-2353
Petrov, A. D., see Chel'tsova, M. A.-920
Petrov, A. D., see Chernyshev, E. A.-593
Petrov, A. D., see Egorov, Iu. P.-3284
Petrov, A. D., see Sadykh-zade, S. I.-1591
Petrov, A. D., see Vdovin, V. M.-2868
Petrov, S. F., see Chlenova, R. S.-3006
Petrova, L. V., see Meshcheriakov, A. P.-2621
Petrova, M. F., see Denisov, S. I.-1925
Petrova, N. I., see Mandel'baum, Ia. A.-469
Petruchenko, M. I., see Kochetkov, N. K.-2288
Piaivinen, E. A., see Gorin, Iu. A.-170
Pigulevskii, G. V., S. A. Kozhin and V. G. Kostenko. Reduction of Limonene Monoxide with Lithium Aluminum Hydride-1471
Pigulevskii, G. V., S. A. Kozhin and V. G. Kostenko. The Problem of the Reduction of 1-Methyl-1-cyclohexene Oxide-1706
Pigulevskii, G. V., and I. N. Naidenova. Methyl Linoleate Monoxide and Its Properties-234
Pigulevskii, V. V., see Mikhailova, V. N.-2302
Pigulevskii, V. V., see Mikhailova, V. N.-3142
Piliugin, G. T., and S. V. Shinkorenko. Research in the Field of Synthetic Dyestuffs. IX. Synthesis of Bisazo Dyes by the Condensation of Diazo Compounds with Salts of N-Aryl Quinaldines-1371
Piliugin, G. T., and S. V. Shinkorenko. Research in the Field of Synthetic Dyestuffs. XI. Condensation of Salts of N-Arylquinaldine with Nitroso Compounds-1378
Piliugin, G. T., E. P. Opanasenko and S. V. Shinkorenko. Research in the Field of Synthetic Dyestuffs. X. Synthesis of N-Aryl-2-β-Anilinovinylquinoline Derivatives and Their Transformations-1374
Pishnamazzade, B., see Mamedov, Shamkhal-1879
Platonova, T. F., A. D. Kuzovkov and P. S. Massagetov. Aconite Alkaloids. IX. Alkaloids of *Aconitum excelsum*-259
Platonova, T. F., A. D. Kuzovkov and P. S. Massagetov. Investigation of Aconite Alkaloids. XIII. The Alkaloids of *Aconitum Rotundifolium* Kar. and Kir. and *Aconitum Nemorum* M. Pop [1]-3157
Platonova, T. F., A. D. Kuzovkov and P. S. Massagetov. Alkaloids of the Chenopodiaceae (Gooseroot). *Anabasis Jazartica* and *Arthrophytum Leptocladum*-3159
Platonova, T. F., A. D. Kuzovkov and P. S. Massagetov. Alkaloids of Plants of the Family of the Asclepiadaceae (milkweed). I. *Antitoxicum Funebre* (Boiss. Et Ky.) Pobed-3162
Plekhan, M. I. Spectrophotometry of Biuret Complexes as a Method of Investigation of Polypeptides and Proteins. XIX. Some Double Decomposition Reactions of Copper-Biuret Complexes-3164
Pletiushkina, A. I., see Topchieva, K. V.-604
Pletiushkina, A. I., see Topchieva, K. V.-614

Pletneva, I. D., see Dokunikhin, N. S.-991
Plisko, E. A. A Search for New Methods of Synthesizing Cellulose Ethers-3242
Plisko, E. A., M. G. Okun', N. M. Grad and N. F. Gintse. The Works of S. N. Danilov in the Field of Cellulose and Its Ethers and Esters-3203
Plisko, E. A., see Danilov, S. N.-2255
Plisov, A. K., and N. V. Bulatova. The Configuration and Properties of Unsaturated Acids and Their Derivatives. VIII. The Reactivity of Erucic and Brassidic Acids and Their Esters-489
Plisov, A. K., and Paladienko, N. P. The Configuration and Properties of Unsaturated Acids and Their Derivatives. IX. The Properties of the α-Methylcrotonic Acids and Their Esters-494
Plotkina, S. A., V. N. Efremova and I. K. Ulezlo. Transformation Reactions of Methylolmethacrylamide-1322
Pochtakova, E. I., see Sokolov, N. M.-1449
Pochtakova, E. I., see Sokolov, N. M.-1455
Pochtakova, E. I., see Sokolov, N. M.-1741
Podberezina, A. S., see Machinskaia, I. V.-1550
Poddubnaia, N. A., and G. I. Lavrenova. Preparation and Investigation of Some Properties of N-Monoaminoacyl Substituted Sarcosine Diketopiperazines-396
Poliker, I. A., see Sidorova, N. G.-1333
Ponomarev, F. G., and Iu. M. Mosichkin. Research in the Field of Unsymmetrical Organic α-Oxides. XVII. Reaction of Pentadienyl Oxide with Ethyl Sodioacetoacetate-2293
Popa, D. P., see Iakovlev, I. P.-2510
Porai-Koshits, B. A., and Ch. Frankovskii. Diamines of Benzimidazole Series. I. Synthesis and Physicochemical Properties of Diamines-902
Porai-Koshits, B. A., and Ch. Frankovskii. Diamines of Benzimidazole Series. II. Substantive Properties of the Azo Dyes Derived from the Diamines-908
Porfir'eva, Iu. I., see Petrov, A. A.-2357
Porfir'eva, Iu. I., see Petrov, A. A.-2362
Postovskii, I. Ia., see Bedniagina, N. P.-361
Postovskii, I. Ia., see Nirenburg, V. L.-198
Potapov, V. M., and A. P. Terent'ev. Stereochemical. Investigations. IV. Schiff Bases from Optically Active α-Benzylethylamine-3349
Potapov, V. M., see Terent'ev, A. P.-1220
Potashnik, A. A., see Kutepov, D. F.-663
Pozharskii, F. T., see Nazarova, Z. N.-1553
Pravova, E. P., see Iakubovich, A. Ia.-316
Pravova, E. P., see Iakubovich, A. Ia.-2325
Preobrazhenskii, N. A., see Chen Chang-pai-3116
Preobrazhenskii, N. A., see Evstigneeva, R. P.-1241
Preobrazhenskii, N. A., see Evstigneeva, R. P.-1246
Preobrazhenskii, N. A., see Evstigneeva, R. P.-2499
Preobrazhenskii, N. A., see Gorbacheva, I. N.-167
Preobrazhenskii, N. A., see Maurit, M. E.-943
Preobrazhenskii, N. A., see Sarycheva, I. K.-630
Preobrazhenskii, N. A., see Tolkachev, O. N.-3345
Priakhina, Z. A., see Maksimov, V. I.-247
Priakhina, Z. A., see Maksimov, V. I.-253
Privezentseva, N. F., see Ginsburg, V. A.-716
Prokof'ev, M. A., see Shvachkin, Iu. P.-1665
Prokof'eva, M., see Derevitskaia, V.-697
Prokof'eva, M., see Derevitskaia, V.-700
Prokof'eva, M., see Derevitskaia, V.-1427
Propp, L. N., see Golodnikov, G. V.-2134
Proskurnina, N. F. Alkaloids of *Salsola Richteri*. VI. Structure of Salsamine-257
Prostakov, N. S., see Nazarov, I. N.-936
Prostakov, N. S., see Nazarov, I. N.-2469
Prostakov, N. S., see Nazarov, I. N.-2771
Protopopova, T. V., and A. P. Skoldinov. β-Acyloxyacroleins-241
Protopopova, T. V., and A. P. Skoldinov. Acetals of β,β-Dihalo-Substituted Propionaldehydes-2466
Protopopova, T. V., and A. P. Skoldinov. β,β-Dihalopropionaldehydes-2829
Ptitsyna, O. A., see Reutov, O. A.-572
Pudovik, A. N., and I. M. Aladzheva. Addition of Ammonia and Amines to Isoprene Oxide-2532
Pudovik, A. N., and L. G. Biktimirova. An Anomalous Reaction of α-Halo Ketones with Esters of Phosphorous Acid. VII. Reactions of Esters of Phosphorous Acid with Chlorinated Derivatives of β-Diketones-1545
Pudovik, A. N., and E. G. Chebotareba. Anomalous Reaction of Phosphites with α-Halo Ketones. VIII. Reactions of Mixed Phosphites with Chloro- and Dichloroacetones-2527
Pudovik, A. N., and L. V. Konovalova. A New Method of Synthesizing Esters of Phosphinic and Thiophosphinic Acids. XXIX. The Addition of Dialkyl Phosphorous Acids to Esters of Vinylacrylic and Sorbic Acids and 3,5 Heptadiene-2-One-1263
Pushkareva, Z. V., and O. N. Nechaeva. Investigation of Heterocyclic N-Oxides. VII. Dipole Moments and Chemical Features of Some Derivatives of Phenazine and Acridine N-Oxides-2729
Pushkareva, Z. V., see Nechaeva, O. N.-2721
Pushkareva, Z. V., see Omel'chenko, S. I.-2733

Rachinskii, F. Iu., N. M. Slavachevskaia and D. V. Ioffe. Mercaptoamines. I. β-Mercaptoethylamine and Its N-Substituted Derivatives-3027
Rachinskii, F. Iu., see Berdichevskii, E. G.-670
Radochina, N. A., see Krasovitskii, B. M.-2520
Radzevenchuk', I. F. Alkylation Over an Aluminosilicate Catalyst Activated by Gaseous Hydrogen Chloride. I. Alkylation of Benzene by Alkyl Chlorides-2461

Rafikov, S.R., see Solomin, A. V.-134
Rall, K. B., see Petrov, A. A.-417
Razbitnoi, V. M., see Iakovlev, G. N.-2653
Razumov, A. I., O. A. Mukhacheva and E. A. Markovich. Derivatives of Alkylphosphonous and Phosphonic Acids. VIII. Synthesis and Properties of Some Alkylated Amides of Alkylphosphonic Chlorides-194
Razumova, N. A., see Petrov, A. A.-1190
Razumova, N. A., see Petrov, A. A.-2171
Razumova, N. A., see Petrov, A. A.-2178
Razumova, N. A., see Petrov, A. A.-3248
Razumovskii, V. V., see Iakubovich, A. Ia.-660
Razumovskii, V. V., see Iakubovich, A. Ia.-1971
Razumovskii, V. V., see Iakubovich, A. Ia.-2329
Razuvaev, G. A., L. M. Bobinova and V. S. Etlis. Organozinc Compounds as Catalysts in the Polymerization of Propylene-1672
Razuvaev and V. N. Lamiaeva. Reactions of Acyl Peroxides with Metals-2270
Razuvaev, G. A., and K. S. Minsker. The Polymeric Peroxide of Vinyl Chloride-957
Razuvaev, G. A., see Etlis, V. S.-1280
Razuvaev, G. A., see Spasskaia, I. F.-1872
Razuvaev, G. A., see Spasskaia, I. F.-3033
Reikhardt, G. F., see Khlopin, N. Ia.-266
Remizov, A. L. Synthesis of Some Adrenalin Derivatives. I. Synthesis of D,L-Adrenalin and Its Analogs-2566
Remizov, A. L. Synthesis of Certain Derivatives of Adrenalin. II. D,L-Adrenochrome Oxime and Semicarbazone-3364
Reutov, O. A., and O. A. Ptitsyna and N. D. Patrina. Double Diazonium Salts of Methyltin Trichloride and Diethyltin Dichloride-572
Riabinin, A. A., and L. G. Matiukhina. The Investigation of Triterpenes. II. The Stucture of Zeorin-2628
Riazanova, K. P., see Krasovitskii, B. M.-2520
Ridel', N. V., and M. P. Gerchuk. Transamination Reactions of Carboxylic Acid Amides-1365
Rodinova, E. P., see Berezovskii, V. M.-1016
Rodionov, V. Ia., see Shemiakin, M. M.-2107
Rodionov, V. M., A. A. Dudinskaia, V. G. Avramenko and N. N. Suvorov. Synthesis of β-Amino Acids from Aromatic Hydroxy and Alkoxyaldehydes-2279
Roge, T. V., and A. A. Balandin. Thermographic Investigation of the Regeneration of Chromium Catalysts-2937
Roginskaia, Ts. N., S. V. Svetozarskii, A. I. Finkel'shtein and E. N. Zil'berman. Molecular Structure of Unsaturated Ketones-Bimolecular Cyclohexanone Condensation Products-2266
Rogovin, Z., see Derevitskaia-697
Rogovin, Z., see Derevitskaia-700
Rogovin, Z., see Derevitskaia-1427
Romadan, I. A., and S. E. Berga. Alkylation of Diphenyl with Alcohols in the Presence of $BF_3 \cdot H_3PO_4$ Catalyst-405
Romanova, N. G., see Voronkov, M. G.-2161
Romazanovich, N. P., see Kretov, A. E.-1029
Rozantsev, E. G., see Iur'ev, Iu. K.-2207
Rozenshtein, S. M., see Iakubovich, A. Ia.-1971
Rozenshtein, S. M., see Iakubovich, A. Ia.-2325
Rozenshtein, S., see Iakubovich, A.-2329
Rozina, D. Sh., L. T. Nesterenko and Iu. I. Vainshtein. On the Synthesis and Structure of the o-Sulfobenzoyl Dichlorides-2904
Rubtsov, M. V., see Chizhov, A. K.-1238
Rubtsov, M. V., see Furshtatova, V. Ia.-650
Rubtsov, M. V., see Iakhontov, L. N.-1234
Rubtsov, M. V., see Iakhontov, L. N.-3139
Rubtsov, M. V., see Iakhontov, L. N.-3146
Rubtsov, M. V., see Mikhlina, E. E.-104
Rubtsov, M. V., see Mikhlina, E. E.-1228
Rubtsova, I. K., see Kotrelev, V. N.-748
Rybakova, M. N., see Lapkin, I. I.-385

Saakian, A. M., see Akopian, A. N.-1276
Sadovaia, N. K., see Iur'ev, Iu. K.-602
Sadovaia, N. K., see Iur'ev, Iu. K.-2200
Sadovaia, N. K., see Iur'ev, Iu. K.-3066
Sadykh-zade and A. D. Petrov. Synthesis and Transformations of Butadienylsilanes-1591
Saiadian, A. G., see Klebanskii, A. L.-554
Saiadian, A. G., see Klebanskii, A. L.-559
Saiadian, A. G., see Klebanskii, A. L.-853
Saiadian, A. G., see Klebanskii, A.L. -3279
Salivon, M. A., see Stepanov, B. I.-1956
Samsonov, G. V., see Funke, V. F.-269
Sarycheva, I. K., G. A. Vorob'eva, N. A. Kuznetsova and N. A. Preobrazhenskii. New Synthesis of 2,6,10,14-Tetramethylhexadecen-15-ol-14, Isophytol-630
Savchuk, E. K., see Vizgert, R.V.-2153
Savel'ev, V. A., see Stepanov, B. I.-2997
Savintsev, P. A., and V. E. Avericheva. Toward the Question of Contact Fusion of Crystals-1748
Savitskaia, M. H., see Koton, M. M.-409
Savushkina, V. I., see Siavtsillo, S. V.-1800
Sedov, L. N., see Fedotova, O. Ia.-753
Semechkina, A. F., and N. N. Shorygina. Investigation of Lignin in Husks of Cotton Seeds-119
Semechkina, A. F., and N. N. Shorygina. Decomposition of Lignin by Metallic Sodium in Liquid Ammonia. VII. Chromatographic Investigation of the Phenols Obtained in the Decomposition of Lignin-3291

Semenov, G. I., see Petrov, A. A.-73
Semenov, G. I., see Petrov, A. A.-417
Semenov, G. I., see Petrov, A. A.-2362
Semenov, L. V., see Chernyshev, E. A.-593
Semenova, N. A., see Abramov, V. S.-3087
Sergeev, P. G., and L. M. Bukreeva. Reaction of Hydrogen Peroxide with Allyl Alcohol and Acrolein in the Presence of Tungstic Acid-101
Sergeev, P. G., and A. M. Sladkov. Auto-oxidation of a Methylene Group Bound to an Aromatic Nucleus. II. Auto-oxidation of the Methyl Ester of 9-Phenylundecanoic Acid-244
Sergeev, P. G., see Fedorova, V. V.-2581
Sergeev, P. G., see Fedorova, V. V.-2586
Sergievskaia, S. I., K. V. Levshina, A. K. Chizhov, A. I. Gavrilova and A. I. Kravchenko. N-Di(chloroethyl)amines of the Alicyclic Series. I.-1884
Sergievskaia, S. I., K. V. Levshina, A. I. Gavrilova and A. K. Chizhov. N-Di(chloroethyl)amines with Alicyclic and Aromatic Radicals in the Molecule. II-1890
Sergievskaia, O. V., see Favorskaia, T. A.-88
Sergievskaia, O. V., see Favorskaia, T. A.-3260
Sergievskaia, S. I., see Sventsitskaia, L. E.-1650
Serkova, V. I., see Venus-Danilova, E. D.-1528
Serova, N. A., and O. S. Madaeva. Steroidal Sapogenines. V. Sapogenines of Leaves of *Agave Americana L.*-2032
Severin, E. S., see Kochetkov, N. K.-3053
Shabanova, M. P., see Kabachnik, M. I.-1618
Shalavina, I. F., see Fabrichnyi, B. P.-2556
Shalavina, I. F., see Gol'dfarb, Ia. L.-213
Shapiro, E. S., see Shostakovskii, M. F.-3337
Shatenshtein, A. I., and E. A. Iakovleva. A Comparison of the Rate of Hydrogen Exchange with Protophilic Solvents-1761
Shatenshtein, A. I., and E. A. Izrailevich. The Proton Mobility of Hydrogen Atoms in Aromatic Hydrocarbons with Aliphatic Substituents-2969
Shavarov, Iu. S., see Levina, R. Ia.-2089
Shchelkunov, A. V., see Martynov, B. F.-3275
Shcherbo, L. I., see Kolensnikov, G. S.-509
Shchukarev, S. A. The Number of Stable Oxides Formed by Metals of the Long Periods of the Periodic System-773
Shchukarev, S. A. Basic and Acidic Oxides of Metals of the Large Periods of the Periodic System-819
Shchukarev, S. A., M. P. Morozova and M. M. Bortrukova. The Enthalpy of Formation of Compounds of Cadmium with Phosphorus, Arsenic and Antimony-3315
Shchukarev, S. A., G. I. Novikov and N. V. Andreeva. The Problem of Thermodynamic Study of Lower Chlorides of Wolfram (Tungsten)-2040
Shchukina, L. A., see Spirichev, V. P.-1758
Shchukina, M. N., see Iashunskii, V. G.-230
Shchukina, M. N., see Markova, Iu. V.-1856
Sheinker, Iu. N., see Suvorov, N. N.-1058
Shemiakin, M. M., M. N. Kolosov, M. G. Karapetian and V. Ia. Rodionov. Studies in the Field of Sarcomycin and Its Analogs. II. Synthesis of Sarcomycin Isomers-2107
Shemiakin, M. M., V. I. Maimind, B. V. Tokarev and V. I. Karpov. Study of the Stephen Reaction-952
Shemiakin, M. M., V. I. Maimind and B. K. Vaichunaite. Study of the Wallach Rearrangement and Related Reactions-1756
Shemiakin, M. M., see Maimind, V. I.-2260
Sherlin, S. M., see Zeide, O. A.-2442
Shevchenko, V. I., and G. I. Derkach. Dimethyl Arylsulfon-N-Methylamidophosphates-1054
Shibaev, L. A., see Iakubchik, A. L.-2095
Shikhiev, I. A., see Shostakovskii, M. F.-1588
Shilov, E. A., see Vainshtein, F. M.-760
Shinkorenko, S. V., see Piliugin, G. T.-1371
Shinkorenko, S. V., see Piliugin, G. T-1364
Shinkorenko, S. V., see Piliugin, G. T.-1378
Shliapochnikov, V. A., see Egorov, Iu. P.-3284
Shorygina, N. N., see Semechkina, A. F.-119
Shorygina, N. N., see Semechkina, A. F.-3291
Shostakovskii, M. F., E. P. Gracheva and N. K. Kul'bovskaia. Synthesis and Transformations of Substituted Vinyl Ethers. VI. Synthesis of α-Methylvinylaryl and α-Methylvinylcyclohexyl Ethers-1308
Shostakovskii, M. F., E. P. Gracheva, and N. K. Kul'bovskaia. Synthesis and Transformations of α-Substituted Vinyl Ethers. VII. Synthesis and Transformations of α-Chloroisopropyl Aryl Ethers-2379
Shostakovskii, M. F., E. P. Gracheva, N. K. Kul'bovskaia. Synthesis and Transformations of α-Substituted Vinyl Ether. VIII. Some Properties of α-Methylvinyl Aryl and α-Methylvinylcyclohexyl Ethers-2382
Shostakovskii, M. F., D. A. Kochkin, V. A. Neterman and F. P. Sidel'kovskaia. Investigations in the Field of the Synthesis and Conversions of Oyxgen-Containing Organosilicon Compounds, On the Interaction of Vinylalkylchlorosilanes with Vinyl Butyl Ether and Vinyl Lactams-2866
Shostakovskii, M. F., and M. R. Kulibekov. Investigation of the Exchange of Oxy-Radicals with Hydrocarbon Radicals of Organomagnesium Compounds. I. Investigation of the Reactivity of Mixed Acetals-563

Shostakovskii, M. F., M. R. Kulibekov. Reaction of Exchange of Hydroxyl Groups for Radicals of Organomagnesium Compounds. II. Reaction of Grignard Reagent with Symmetric Acetals-926
Shostakovskii, M. F., and M. R. Kulibekov. Investigation of the Exchange of Oxy Radicals for the Hydrocarbon Radicals of Organomagnesium Compounds. IV. Interaction of Grignard Reagents with Organic Acylals-2376
Shostakovskii, M. F., M. R. Kulibekov and I. A. Shikhiev. Investigation of the Exchange Reaction of Oxy Radicals with Radicals of Organomagnesium Compounds. III. Interaction of Organomagnesium Compounds with Mixed Organosilicon Acetals-1588
Shostakovskii, M. F., M. R. Kulibekov and A. K. Gorban'. Synthesis of β-Chloroethyl Phenyl Acetal-2862
Shostakovskii, M. F., M. R. Kulibekov and A. K. Gorban'. Synthesis of γ,γ'-Diphenyldipropyl Acetal-2864
Shostakovskii, M. F., E. S. Shapiro and E. V. Dubrova. Synthesis of Polyfunctional Sulfur Compounds from Divinyl Ether and Hydrogen Sulfide-3337
Shostatskaia, I. D., see Iakubchik, A. I.-3121
Shpital'nyi, A. S., and N. S. Iablochnik. On the Process of Formation of Polyamide Resins. VIII. The Question of the Alkaline Polymerization of ε-Caprolactam-3307
Shpital'nyi, A. S., and Kharit, Ia. A. The Process of Polyamide Resin Formation. VII. The Composition and Structure of Salts Formed by Dicarboxylic Acids and Diamines or Hydrazine-2715
Shtifman, L. M., S. V. Siavtsillo and L. G. Kuriakova. The Polarographic Determination of Some Derivatives of 2-Ethylanthraquinone-2066
Shuikin, N. I., see Nekrasova, V. A.-15
Shusherina, N. P., see Lur'e, M. Iu.-1410
Shvachkin, Iu. P., M. A. Prokof'ev. Synthesis of Phosphoramidopyrimidines-1665
Shvarts, E. Iu., see Petrov, A. A.-1490
Shvedov, V. I., see Grinev, A. N.-439
Shvesova-Shilovskaia, K. D., see Mel'nikov, N. N.-464
Shvetsova, L. S., see Zavgorodnii, S.V.-2695
Shamkhal Mamedov and D. Khydyrov. Ethers of Glycols and Their Derivatives. XXXV. Synthesis of β,γ-Dibromo Derivatives of Ethers of Methylene Glycol-2836
Shatenshtein, A. I., and A. V. Vedeneev. Hydrogen Exchange of Phenol and Its Ethers with Solutions of Potassamide in Liquid Deuteroammonia-2672
Shatenshtein, A. I., A. V. Vedeneev and P. P. Alikhanov. Hydrogen Exchange in Phenols, Its Ethers and Aromatic Amines with Liquid DBr-2666
Siavtsillo, S. V., V. I. Savushkina and E. M. Zhernovskaia. Synthesis of 2-Ethylanthrone and 2-Ethyl-10-oxanthrone Labeled with Carbon C^{14} in the Nucleus and a Study of Some of Their Properties-1800
Siavtsillo, S. V., see Shtifman, L. M.-2066
Sidel'kovskaia, F. P., see Shostakovskii, M. F.-2866
Sidorov, I. A., see Lutskii, A. E.-2423
Sidorova, N. G., and I. A. Poliker. Cycloalkylation of Aromatic Compounds. XIV. Condensation of Cyclohexanol with Some Aromatic Hydrocarbons-1333
Sidorova, N. G., and G. Kh. Tyshchuk. Cycloalkylated Aromatic Compounds. XV. The Condensation of Fluorene with Cyclohexanol in the Presence of Aluminum Chloride-2069
Sigov, O. V., I. F. Baev. Synthesis of 1,4-Diisopropylbenzene and Some of Its Transformations-1337
Simolin, A. V., see Levina, R. Ia.-2347
Simon, I. V. The Synthesis of Substances with a Hypotensive Action-Derivatives of Quaternary Ammonium Bases. IV. Quaternary Salts of β-Phenylisopropyldimethylamine-2619
Simonov, A. M. Dipolar Ions Formed by the Elimination of a Proton from an NH Group. XII. Derivatives of 6-Quinolinesulfonic Acid-976
Skanavi-Grigor'eva, M. S., and V. I. Staroverova. Investigation of Anode Deposits Formed in the Electrolysis of Solutions of Certain Thallium Salts-1737
Skoldinov, A. P., see Protopopova, T. V.-241
Skoldinov, A. P., see Protopopova, T. V.-2466
Skoldinov, A. P., see Protopopova, T. V.-2829
Skripach, T. K., see Baranaev, M. K.-1678
Sladkov, A. M. Utilization of Benzene as a Solvent in Acetylation Reaction According to Friedel-Crafts-1791
Sladkov, A. M., and L. K. Luneva. Preparation of Hydratropic Alcohol-2921
Sladkov, A. M., see Sergeev, P. G.-244
Slavachevskaia, N. M., see Rachinskii, F. Iu.-3027
Smagina, E. I., see Ormont, B. F.-281
Smetankina, N. P., see Petrov, A. D.-2122
Smirnova, O. V., see Losev, I. P.-359
Smirnova, O. V., see Losev, I. P.-964
Smirnova, O. V., see Losev, I. P.-968
Smol'ianinova, E. K., see Svadkovskaia, G. E.-2305
Soborovskii, L. Z., B. M. Gladshtein, M. I. Kiseleva and V. N. Chernetskii. Studies of Organic Sulfur Compounds. I. The Synthesis of Alkanesulfonyl Fluorides and Their Halogen Derivatives-1909

Soborovskii, L. Z., B. M. Gladshtein, V. N. Chernetskii and M. I. Kiseleva. Studies of Organic Sulfur Compounds. II. The Synthesis of Alkenesulfonyl Fluorides and Their Halogen Derivatives-1913
Soborovskii, L. Z., see Baranaev, M. K.-1678
Soborovskii, L. Z., see Bruker, A. B.-347
Soborovskii, L. Z., see Bruker, A. B.-2450
Soborovskii, L. Z., see Gladshtein, B. M.-2145
Soborovskii, L. Z., see Iakubovich, A. Ia.-313
Soborovskii, L. Z., see Zinov'ev, Iu. M.-1600
Sokolov, N. M., and E. I. Pochtakova. The Irreversible-Reciprocal System from Sodium and Potassium Formates and Thiocyanates-1449
Sokolov, N. M., and E. I. Pochtakova. The Irreversible-Reciprocal System of Sodium and Potassium Acetates and Propionates-1455
Sokolov, N. M., and E. I. Pochtakova. Irreversible-Common System of Sodium and Potassium Butyrates and Thiocyanates-1741
Sokolov, N. M., see Dmitrevskaia, O. I.-2949
Sokolov, N. M., see Tsindrik, N. M.-1462
Sokolov, N. M., see Tsindrik, N. M.-1775
Sokolov, N. N. Investigations in the Field of Organocyclosiloxanes. III. The Use of the Method of Thermooxidative Destruction for the Investigation of the Hydrolysis Products of Alkyltrichlorosilane-2611
Sokolova, N. N. Investigation in the Field of Organocyclosiloxanes. IV. Reactivity of Organocyclosiloxanes in Dependence on the Number of Links in the Cycle-3354
Sokolova, T. A., and L. A. Ovsiannikova. The Synthesis of N-Substituted Methacrylamides. IV. Acylation of Aromatic Amines with Methacrylyl Chloride in an Aqueous Medium-757
Sokolova, T. A., see Koton, M. M.-409
Solomin, A. V., B. V. Suvorov and S. R. Rafikov. Oxidation of Organic Compounds. XV. Vapor-Phase Oxidation of Ethylbenzene on Tin Vanadate-134
Solonskaia, N. T., see Blizniukov, V. I.-1293
Sopov, N. P., and M. L. Kovner. The Condensation of Diene Hydrocarbons with Cinnamaldehyde. The Synthesis of Hydroaromatic Alcohols, Acetates and Hydrocarbons-2184
Sopova, A. S., see Perekalin, V. V.-656
Sorokina, N. P., see Suvorov, N. N.-1058
Spasskaia, I. F., V. S. Etlis and G. A. Razuvaev. The Chlorination of Ethylene Glycol-1872
Spasskaia, I. F., V. S. Etlis and G. A. Razuvaev. Chlorination of Olefin Chlorohydrins-3033
Spasskova, A. I., see Iakubchik, A. L.-143
Spasskova, A. I., see Iakubchik, A. I.-890
Spasskova, A. I., see Iakubchik, A. I.-2095
Spasskova, A. I., see Iakubchik, A. I.-3121
Speranskaia, V. A., see Farberov, M. L.-2190
Spirichev, V. P., and L. A. Shchukina. Synthesis of L-Acetylalanine from D,L-Alanine-1758
Spiridonova, T. G., see Bruker, A. V.-347
Spryskov, A. A., and Iu. G. Erykalov. Orientation in Aromatic Ring Substitution. III. Isomerization of Dichlorobenzenes-1688
Spryskov, A. A., and O. I. Kachurgin. The Study of Sulfonation Reaction. XLVII. The Study of Chloro-Benzenesulfonic Acid Hydrolysis with the Use of Radioactive Indicator-1693
Spryskov, A. A., and O. I. Kachurgin. Orientation in Substitution in the Aromatic Nucleus. IV. Sulfonation of Chlorobenzene-2250
Spryskov, A. A. and Iu. L. Kuz'mina. Sulfonation Reaction. XLVI. Equilibrium Between Toluenetrisulfonic Acid and Its Trichloride-185
Sobolev, Iu. P., see Berezovskii, V. M.-262
Staroverova, V. I., see Skanavi-Grigor'eva, M. S. -1737
Stepanov, B. I. The Replacement of Halogen in Azo Compounds. IV. The Replacement of Chlorine in 5-Methyl-2-chlorobenzeneazo-2'-naphthol by Alkoxy and Aroxy Groups and the Preparation of Ethers of 3-Amino-4-hydroxytoluene-2705
Stepanov, B. I., and M. A. Andreeva. Replacement of Halogen in Azo Compounds. III. Preparation of Derivatives of o-Arylalkoxyanilines-2525
Stepanov, B. I., L. A. Dediukhina and T. T. Strashnova. Replacement of Halogen in Azo Compounds. II. Reaction of 2-Chlorophenylazo-2'-naphthol with Phenolates-1962
Stepanov, B. I., M. A. Salivon, V. F. Lagidze and L. A. Dediukhina. Replacement of Halogen in Azo Compounds. I. Replacement of Chlorine in 2-Chlorophenylazo-2'-naphthol by Alkoxy Groups-1956
Stepanov, B. I., and V. A. Savel'ev. Halogen Displacement in Azo Compounds. VI. Substitution of Chlorine by a Methoxy Group in 2-Hydroxy-8-Chloro(1,1')-Azonaphthalene and in Its Copper Complex-2997
Stepanov, B. I., see Andreeva, M. A.-2995
Stepanov, F. N., and S. L. Davydova. Heterocyclic Derivatives of Methyl Ketones-864
Strashnova, T. T., see Stepanov, B. I.-1962
Strepkov, S. M. Study of the Structure of Some Fructosans of Plants of the Family Lilaceae-3173
Strukov, I. T. The Condensation of Methyl Esters of α-Amino-β-Mercaptocarboxylic Acids with Bromopyruvic Acid-71
Sukhinin, N. P., see Martynov, V. F.-2113
Sukhomlinov, A. K. The Tautomerism of 9-Aminoacridine-1009
Sukhomlinov, A. K., see Blizniukov, V. I.-1301

Sukhomlinov, A. K., see Blizniukov, V. I.-1659
Sukhomlinov, A. K., see Blizniukov, V. I.-1662
Sultanov, A. S., M. F. Abidova and V. A. Maslennikova. Catalytic Reduction of Benzaldehyde-765
Sumarokova, T. N., see Iarmukhamedova, E. Sh.-1468
Suvorov, B. V., see Solomin, A. V.-134
Suvorov, N. N., and A. A. Dudinskaia. Thyroid Gland Hormones and Their Analogs. II. Synthesis of Isomers of Betazine-1430
Suvorov, A. A., A. A. Dudinskaia and L. M. Morozovskaia. Thyroid Gland Hormones and Their Analogs. III. Synthesis of Amino Analogs of Betazine-1433
Suvorov, N. N., L. M. Morozovskaia and A. A. Dudinskaia. Hormones of the Thyroid Gland and Their Analogs. IV. The Synthesis of Desamino Analogs of Betazine (β-Diiodotyrosine)-2634
Suvorov, N. N., N. P. Sorokina and Iu. N. Sheinker. Investigations in the Field of Indole Derivatives -1058
Suvorov, N. N., see Nikiforova, O. K.-2025
Suvorov, N. N., see Rodionov, V. M.-2279
Svadkovskaia, G. E., E. K. Smol'ianinova and V. N. Belov. Preparation of ω-Hydroxypentadecanoic Acid by the Method of Electrolytic Cross Condensation. II.-2305
Sventsitskaia, L. E., A. A. Kropacheva and S. I. Sergievskaia. 2,4-Di(ethyleneimino)-1,3,5-triazines-1650
Svetkin, Iu. V. Reaction of Ketene with Nitrogen-Containing Bases. V. Acetylation of Bipiperidine with Ketene-692
Svetkin, Iu. V. The Reaction of Ketene with Nitrogen-Containing Bases. VI. The Mechanism of the Acetylation of Amines with Ketene-694
Svetkin, Iu. V., and G. Kretsu. The Reaction of Ketene with Nitrogen-Containing Bases. VII. Chloroacetylation of Primary Amines-1907
Svetozarskii, S. V., see Roginskaia, Ts. N-2266

Tatevskii, B. M. New Regularities in the Physicochemical Properties of Hydrocarbons. III. Heats of Crystallization of n-Alkanes-2965
Tatevskii, V. M., and V. A. Benderskii. New Regularities in the Physicochemical Properties of Hydrocarbons. II-1781
Temnikova, T. I., A. N. Anikeeva and N. S. Tikhomirova-Sidorova. The Works of S. N. Danilov in the Field of Isomeric Conversions and Molecular Rearrangements of Carbonyl and Hydroxycarbonyl Compounds and Carbohydrates and Their Theoretical Importance-3194
Temnikova, T. I., and N. A. Oshueva. Chemical Conversions of α-Bromocyclohexanone-3252
Teng Jun-hsiang, see Khaletskii, A. M.-2393
Teng Jun-hsiang, see Khaletskii, A. M.-3057
Teng Jun-hsiang, see Pesin, V. G.-2841
Teng Jun-hsiang, see Pesin, V. G.-3060
Teng Jun-hsiang, see Pesin, V. G.-3300
Terent'ev, A. P., and R. A. Gracheva. Preparation of α-Amino Acid Via Furan Derivatives-1225
Terent'ev, A. P., and Ia. D. Mogilianskii. The Complex Pyridine-Cuprous Chloride As an Autoxidation Catalyst. I. Preparation of Azo Compounds from Primary Aromatic Amines-2002
Terent'ev, A. P., and V. M. Potapov. Stereochemical Investigations. III. Schiff Bases from Optically Active α-Phenylethylamine-1220
Terent'ev, A. P., M. A. Volodina and V. G. Mishina. Synthesis of Pyrrolidine Bases from γ-Ketoalcohols-222
Terent'ev, A. P., M. A. Volodina and V. G. Mishina. Synthesis and Properties of Pyrrolidine Bases. IV. 2-Methyl-N-β-aminoethylpyrrolidine and Some of Its Transformations-1566
Terent'ev, A. P., see Grinev, A. N.-77
Terent'ev, A. P., see Grinev, A. N.-439
Terent'ev, A. P., see Grinev, A. N.-1894
Terent'ev, A. P., see Grinev, A. N.-1897
Terent'ev, A. P., see Grinev, A. N.-1900
Terent'ev, A. P., see Iurkevich, A. M. -226
Terent'ev, A. P., see Potapov, V. M.-3349
Tetiueva, L. A., and P. A. Petiunin. Reactions of Magnesylamines. IV. Arylamidation of Aromatic Aldehydes with the Help of Arylamine-N,N-Dimagnesium Halides-719
Tetiueva, L. A., see Petiunin, P. A.-1072
Tetiueva, L. A., see Petiunin, P. A.-1596
Tikhomirov, B. I., see Iakubchik, A. I.-890
Tikhomirova-Sidorova, N. S., and G. E. Ustiuzhanin. Amino Derivatives of 1,4-Anhydroxylitol-3238
Tikhomirova-Sidorova, N. S., see Temnikova, T. I.-3194
Tikhonova, G. V., see Kretov, A. E.-2832
Tiniakova, E. I., E. K. Khrennikova and B. A. Dolgoplosk. Reactions of Free Radicals in Solution. XIV. Formation of Free Radicals in Decomposition of Hydrogen Disulfide and Their Reactions with α- and β-Olefins-1682
Tiniakova, E. I., E. K. Khrennikova and B. A. Dolgoplosk. On the Mechanism of Action of Accelerators of the Process of Sulfur Vulcanization-3295
Tishchenko, V. V., and V. F. Kazanskaia. Conversion of Δ^3-p-Menthene on Gumbrine-2313
Tishchenko, V. V., and N. S. Lishenkova. Thermocatalytic Transformation of α-Terpinene Over Gumbrin-1999
Titov, A. I., and F. L. Makliaev. A Discussion. In Reply to the "Remarks" by E. A. Shilov [1]-551

Titov, V. V., see Iur'ev, Iu. K.-3066
Tiurina, L. N., see Al'perovich, M. A.-2573
Tokarev, B. V., see Shemiakin, M. M.-952
Tolkachev, O. N., V. G. Voronin and N. A. Preobrazhenskii. Synthesis of Bromo-Substituted β-Phenylethylamines-3345
Tolstikov, G. A., see Volkova, V. S.-2140
Tonova, V. A., see Topchieva, K. V.-614
Topchieva, K. V., A. I. Pletiushkina and I. A. Zen'kovich. Conversion of Allylbenzene Over Aluminosilicate Catalysts. I. Study of Conversion Kinetics-604
Topchieva, K. V., A. I. Pletiushkina and V. A. Tronova. Conversion of Allylbenzene Over Aluminosilicate Catalysts. II. Structure and Mechanism of Formation of the Dimer-614
Torf, S. F., and N. V. Khromov-Borisov. Diphensuccindane and 2,6-Dihydroxydiphensuccindane-2488
Treshchova, E. G., see Levina, R. Ia.-2347
Trifonov, N. A., see Dianov, M. P.-845
Trofimova, T. A., see Boldyrev, B. G.-1981
Troshchenko, A. T. Investigation of Acridine Derivatives. 1. Synthesis of 1-Nitro-2-methoxy-9-chloroacridine-2245
Trubnikov, I. S., see Lur'e, M. Iu.-1410
Tsindrik, N. M. Ternary Reciprocal System of Lithium and Sodium Formates and Nitrates-806
Tsindrik, N. M., and N. M. Sokolov. The Ternary System from Lithium and Sodium Propionates and Nitrates-1462
Tsindrik, N. M., and N. M. Sokolov. Ternary Conjugate System of Lithium and Sodium Butyrates and Nitrates-1775
Tsitokhtsev, V. A., see Iakubchik, A. I.-143
Tsukervanik, I. P., and Z. Ia. Belinson. The Condensation of Benzotrichloride with Benzene in the Presence of Aluminum Chloride-2077
Tsukervanik, I. P., see Grebeniuk, A. D.-2417
Tsukervanik, I. P., see Mel'kanovitskaia, S. G.-10
Tsukervanik, I. P., see Mel'kanovitskaia, S. G.-2071
Tsukshverdt, T. V., see Dolgov, B. N.-2741
Tsvetkova, N. K., and D. E. Dionis'ev. Investigation of the Interaction of Diphenylamine with Organic Acids by the Methods of Physicochemical Analysis-840
Tsvetkova, N. K., and D. E. Dionis'ev. Investigation of the Reaction of Phenyl-β-Naphthylamine with Organic Acids by the Methods of Physicochemical Analysis-1750
Tumanova, A. V., see Dolgopol'skii, I. M.-1829
Turitsyna, N. F., see Vompe, A. F.-2891
Turkevich, N. M., and E. V. Vladzimirskaia. Synthesis of Thiazolidone Derivatives Having Biological Interest. VIII. Replacement of Some Radicals of Oxo-Compounds by Others in the Molecules of Derivatives of Thiazolidinedione-2,4-Hydrazone-2-1260
Tyshchuk, G. Kh., see Sidorova, N. G.-2069

Udovenko, V. V., and Iu. Ia. Fialkov. The Viscosity of Binary Systems with Exchange Interaction-791
Ukhova, L. I., see Bardyshev, I. I.-532
Ulezlo, I. K., see Plotkina, S. A.-1322
Usovskaia, V. S., see Nikitskaia, E. S.-161
Uspenskaia, I. N., see Motsarev, G. V.-1395
Ushenko, I. K., and S. E. Gornostaeva. Studies in the Field of the Chemistry of the Cyanine Dyes. XIII. Thiacyanines which Contain Unsaturated Radicals as Substituents in the 6,6'-Positions of Benzthiazole-1717
Ushenko, I. K., see Al'perovich, M. A.-2573
Ustiuzhanin, G. E., see Tikhomirova-Sidorova, N. S.-3238
Utkin, L. M., see Koretskaia, N. I.-1056
Utkin, L. M., see Labenskii, A. S.-3150

Vaichunaite, B. K., see Shemiakin, M. M.-1756
Vainshtein, F. M., and E. A. Shilov. Sulfolysis of the Sulfonyl Groups in Aromatic Sulfonic Acids-760
Vainshtein, Iu. I., see Rozina, D. Sh.-2904
Vanags, E., see I. Zalukaev-474
Vanag, G. Ia., and V. P. Oshkaia. 4-Nitro-1,3-indanedione-1570
Vanag, G. Ia., see Geita, L. S.-2825
Vanag, G. Ia., see Gudrinietse, E. Iu.-59
Vanag, G. Ia., see Gudrinietse, E. Iu.-95
Vanag, G. Ia., see Matskanova, M. A.-2822
Vanag, G. Ia., see Neiland, O. Ia.-1256
Vanag, G. Ia., see Ozol, Ia. I.-3114
Variukhina, L. V., see Khmelevskii, V. I.-2016
Varnakova, L. P., see Gorbacheva, I. N.-167
Vartanian, S. A., see Nazarov, I. N.-2781
Vasileiskaya, N. S. Reactions of Polyhalogen Compounds with Alcohols-1786
Vasil'eva, A. S., see Iarovenko, N. N.-2539
Vasil'eva, M. N., see Berlin, A. Ia.-1033
Vasilevskaia, T. V., see Ol'dekop, Iu. A.-3037
Vasiutina, Zh. D., see V. F. Martynov-583
Vas'kovskii, V. E., see Iur'ev, Iu. K.-3288
Vdovin, V. M., and A. D. Petrov. Synthesis of Alkenyl-α-CN-Isopropoxysilanes-2868
Vdovina, R. G., see Maimind, V. I.-2260
Vedeneev, A. V., see Shatenshtein, A. I.-2666
Vedeneev, A. V., see Shatenshtein, A. I.-2672
Velichko, S. A., see Gavrilov, V. G.-2138
Venevtseva, N. K., see Grinev, A. N.-1894
Venevtseva, N. K., see Grinev, A. N.-1897

Venevtseva, N. K., see Grinev, A. N.-1900
Venus-Danilova, E. D., and V. I. Serkova. Investigation of Transformations of Pinacols with Substituted Acetylenic Radicals. XVI. Synthesis and Transformations of Sym. Dimethylphenyl(tertbutylethynyl) Ethylene Glycol (3,6,6-Trimethyl-2-phenylheptyn-4-diol-2,3)-1528
Venus-Danilova, E. D., see Fabritsy, A.-3255
Venus-Danilova, E. D., see Pavlova, L. A.-634
Verezin, I. V., B. I. Makalets and L. G. Chuchukina. The Mechanism of Acid Oxidation by Molecular Oxygen in an n-Heptane Medium-2746
Vertiulina, L. N., and N. I. Maliugina. Reduction of Nitrophenols at a Multidrop Mercury Cathode-301
Veselkova, E. G., see Bekhevkin, I. M.-795
Veselovskaia, L. K., see Kozlov, V. V.-3359
Vilesova, M. S., see Klebanskii, A. L.-1036
Vilesova, M. S., see Klebanskii, A. L.-1042
Vilesova, M. S., see Klebanskii, A. L.-1574
Vilesova, M. S., see Klebanskii, A. L.-1578
Vilesova, M. S., see Klebanskii, A. L.-1815
Vilesova, M. S., see Klebanskii, A. L.-1820
Vilesova, M. S., see Klebanskii, A. L.-1824
Vinogradov, V. P., see Nazarov, I. N.-451
Vizgert, R. V. The Hydrolysis of Esters of Aromatic Sulfonic Acids. V. The Hydrolysis of Esters of Benzenesulfonic Acid and Substituted Phenols-1917
Vizgert, R. V., and E. K. Savchuk. Hydrolysis of Aromatic Sulfonic Acid Esters. VI. Alkaline and Aqueous Hydrolysis of Nitro-Substituted Aryl Sulfonates-2153
Vizgert, R. V., and Ia. P. Berkman. Reactions of Aromatic Sulfonic Acid Esters. VII. Arylating Properties of Dinitrophenyl Benzenesulfonate-2158
Vizgert, R. V., see Baranov, S. N.-1330
Vitt, S. V., see Parnes, Z. N.-402
Vladzimirskaia. E. V. Synthesis of Thiazolidone Derivatives of Biological Interest. IX. Synthesis of 3-Derivatives of 2,4-Thiazolidinedione Hydrazone-1555
Vladzimirskaia, E. V., see Turkevich, N. M.-1260
Vlasova, R. Ia., see Lapkin, I. I.-930
Volkov, V. P., see Iur'ev, Iu. K.-2408
Volkova, V. S., and G. A. Tolstikov. The Problem of the Hydrogen Bond in Meconic Acid-2140
Volodina, M. A., see Terent'ev, A. P.-222
Volodina, M. A., see Terent'ev, A. P.-1566
Volodkovich, S. D., N. N. Mel'nikov, A. F. Plate and Prianishnikova. Organic Insectofungicides. XXXV. Reaction of 1,1-Difluorotetrachlorocyclopentadiene with some Unsaturated Compounds-3153
Volodkovich, S. D., see Mel'nikov, N. N.-3342
Vol'pin, M. E., I. S. Akhrem and D. N. Kursanov. Effect of Nucleophilicity of the Anion on the Character of Bonding in Compounds of Tropylium-326
Vompe, A. F., and N. F. Turitsyna. Reactions of Pyridinium Salts. II. Interaction of Chloro-2,4-dinitrophenylates of Substituted Pyridine Bases with Aniline-2891
Vorob'ev, V. D., see Petrov, A. D.-1809
Vorob'ev, V. D., see Petrov, A. D.-2353
Vorob'eva, G. A., see Sarycheva, I. K.-630
Voronin, V. G., see Tolkachev, O. N.-3345
Voronkov, M. G., V. P. Davydova and A. N. Lazarev. Investigations in the Field of Alkoxysilanes. XII. Hexa-tertiary-butoxycyclotrisiloxane-2167
Voronkov, M. G., and N. G. Romanova. The Thermal Addition of Trichlorosilane to Diolefinc Hydrocarbon-2161
Voronkov, M. G., see Borisov, S. N.-3318
Voronkov, M. G., see Davydova, V. P.-1922
Vorozhtsov, N. N., Jr., and G. G. Iakobson. Preparation of 2,4-Dinitrophenyl Derivatives of Hydroxy and Mercapto Compounds and Amines-40
Vorozhtsov, N. N., Jr. and V. A. Koptiug. Catalytic Conversions of Halogen Derivatives of the Aromatic Series. IV. A Study of the Mechanism of the Catalytic Isomerization of Monochloronaphthalenes Using Labeled Atoms-368
Vorozhtsov, N. N., Jr., and V. A. Koptiug. Mechanism of α-Tetraloxime Conversion into α-Naphthylamine-1697
Vorozhtsov, N. N., Jr., and V. A. Koptiug. Dehydrogenation of α-Tetralone with Selenium and Synthesis of 1-Naphthol-1 C^{14}-3010
Vorozhtsov, N. N., Jr., and S. I. Kutkevichus. Investigation of the Products from the Reaction of Epichlorohydrin and Aromatic Amines. III. The Action of Hydrochloric Acid and Thionyl Chloride on 3-Hydroxy-1,2,3,4-Tetrahydro-7,8-benzoquinoline and on 3-Hydroxy-1,2,3,4-tetrahydro-5,6-benzoquinoline-2710
Vostrukhina, Z. N., see Iakubovich, A. Ia.-1971
Vovsi, B. A., and A. A. Petrov. Investigation of Conjugated Systems. LXXXVII. Addition of α-Chloro- and α-Bromo-Ether to Chloroprene-1481
Vul'fson, N. S., and V. I. Zaretskii. Investigation in the Field of the Dieckmann Reaction. III. Cyclization of the Diethyl Ester of α-Methylpimelic Acid-365
Vul'fson, N. S., and V. I. Zaretskii. A Study in the Field of the Dieckmann Reaction. V. Cyclization of Diethyl Ester of α-Carbethoxypimelic Acid-1951
Vul'fson, N. S., see Zaretskii, V. I.-382
Vysokosov, A. N., see Iur'ev, Iu. K.-1361
Vysokosov, A. N., see Iur'ev, Iu. K.-1603
Vysokosov, A. N., see Iur'ev, Iu. K.-2793

Zagorevskii, V. A. A Study of the Effect of the Reagent's Character on the Direction of O- and C-Substitution of Metal Derivatives of a Keto-Enol System-480
Zaitsev, I. A., see Grinev, A. N.-439
Zaitsev, I. A., see Grinev, A. N.-1897
Zaitseva, E. L., see Iur'ev, Iu. K.-2203
Zak, A. G., see Iakubchik, A. I.-3121
Zakharova, A. I., and A. M. Efros. The Cyanoethylation of Acetylene γ-Glycols-3270
Zalukaev, L., and Vanags, E. Some Reactions of 2-Nitromethylquinoline. I. Salt Formation and the Action of Halogens-474
Zarankina, Ts. D., see Evstigneeva, R. P.-1246
Zaretskii, V. I., and N. S. Vul'fson. Investigation in the Field of the Dieckmann Reaction. IV. Cyclization of the Tetraethyl Ester of 2-Methylpentanetetracarboxylic-1,1,5,5-Acid-382
Zaretskii, V. I., see Vul'fson, N. S.-365
Zaretskii, V. I., see Vul'fson, N. S.-1951
Zarubinskii, G. M., see Anikeeva, A. N.-3233
Zasechkina, Z. P., see Korshak, V. V.-2874
Zaslavskii, I. I. Nuclear (Atomic) Concentration and Specific Gravities of Hydrocarbons-788
Zavel'skii, D. Z., and L. A. Lishnevskaia. Reaction of Diazo Compounds with Sulfamic Acid and Its Derivatives. VII. Reaction of Diazo Compounds with Unsubstituted Sulfamic Acid-726
Zavel'skii, D. Z., and L. A. Lishnevskaia. Reactions of Diazo Compounds with Sulfamic Acid and Its Derivatives. VIII. Diazonium Salts of Arylsulfamic Acids-735
Zavel'skii, D. Z., and L. A. Lishnevskaia. Reaction of Diazo Compounds with Sulfamic Acid and Its Derivatives. IX. Reasons for the Color of Diazonium Salts of Arylsulfamic Acids-983
Zavel'skii, D. Z., and L. A. Lishnevskaia. Reaction of Diazo Compounds with Sulfamic Acid and Its Derivatives. X. Concerning Colored Salts of Acylaminoarylsulfonic Acids with Diazonium Bases-1966
Zavel'skii, D. Z., and L. A. Lishnevskaia. Reaction of Diazo Compounds with Sulfamic Acid and Its Derivatives. XI. Causes of the Coloration of Some Diazonium and Heterocyclic Ammonium Salts-2594
Zavel'skii, D. Z., and L. A. Lishnevskaia. Reaction of Diazo Compounds with Sulfamic Acid and Its Derivatives. XII. Diaryltriazene-N-sulfonic Acids and Their Diazonium Salts-2602
Zavel'skii, D. Z., see Baranchik, N. M.-1400
Zavgorodnii, S. V., and L. S. Shvetsova. Alkylation of Isopropylbenzene by Pseudobutylene in the Presence of $BF_3 \cdot H_3PO_4$-2695
Zdanovich, V. S., see Blokh, G. A.-2680
Zeide, O. A., S. M. Sherlin and A. B. Bruker. Reaction of p-Halophenylhydrazines with Arsenic Acid-2442
Zeinalov, B. K., see Mamadov, Shamkhal-1876
Zelmen, V. N., see Ozol, Ia. K.-3114
Zenkova, L. N., see Markova, Iu. V.-1856
Zenkova, R. A., see Iakovlev, G. N.-2653
Zen'kovich, I. A., see Topchieva, K. V.-604
Zhdanov, Iu. A. Further Discussion. The Problem of the General Definition of Chemistry-2643
Zhenodarova, S. M., see Morozova, E. A.-1708
Zhenodarova, S. M., see Morozova, E. A.-1711
Zhernovskaia, E. M., see Siavtsillo, S. V.-1800
Zhmurova, I. N., see Kirsanov, A. V.-2514
Zhoglo, F. A., see Baranov, S. N.-1330
Zhukova, I. G., see Iur'ev, Iu. K.-5
Zil'berman, E. N., see Roginskaia, Ts. N.-2266
Zinov'ev, Iu. M., and V. N. Kulakova and L. Z. Soborovskii. Synthesis of Organophosphorus Compounds from Hydrocarbons and Their Derivatives. VII. Oxidative Chlorophosphonation by Means of Alkyl and Dialkylamidophosphorodichloridites-1600
Zinov'ev, Iu. M., see Baranaev, M. K.-1678
Zin Shin-yung, see Ch'ih Yueh-fon-1542
Zoborovskii, L. A., see Gladshtein, B. M.-2454
Zolotov, Iu. M., see Kirsanov, A. V.-340
Zvontsova, A. S., see Kaplan, S. Z.-3310

JOURNAL OF GENERAL CHEMISTRY OF THE USSR

Volume 28, Number 1 January 1958

CONTENTS

	PAGE	RUSS. PAGE
Tetraacyloxysilanes in Organic Synthesis. XIII. Synthesis of N,N-Diethylamides and N-Arylamides of Acids with the Aid of Silicoanhydrides of Saturated Monobasic Organic Acids. Iu. K. Iur'ev and Z. V. Beliakova	1	3
Catalytic Conversions of Heterocyclic Compounds. LIII. Conversion of Homologs of Oxazole to Homologs of Thiazole. Iu. K. Iur'ev and I. G. Zhukova	5	7
Radical and Ion Alkylation of the Aromatic Ring. VI. Reactions of Diphenylchloromethane with Toluene and Benzene. S. G. Mel'kanovitskaia and I. P. Tsukervanik	10	11
Chlorination of Five- and Six-membered Cyclanes. V. A. Nekrasova, N. I. Shuikin and S. S. Novikov	15	15
Studies in the Field of the Chemistry of 2,1,3-Thiodiazole. VI. Chlorination and Bromination of 4- and 5-Aminobenzo-2,1,3-thiodiazoles. V. G. Pesin and A. M. Khaletskii	20	20
The Chemistry of Processes of Far-Reaching Chlorination of Pentane. L. M. Kogan, N. M. Burmakin and N. V. Cherniak	27	27
The Reaction of Phosphorus Pentachloride with Esters of Oxamic Acid. Amides of Alkoxydichloroacetic Acids. A. V. Kirsanov and V. P. Molosnova	31	30
Diesters of Arylamidophosphoric Acids. A. V. Kirsanov and R. G. Makitra	35	35
Preparation of 2,4-Dinitrophenyl Derivatives of Hydroxy and Mercapto Compounds and Amines. N. N. Vorozhtsov, Jr., and G. G. Iakobson	40	40
Radiochemical Investigation of Reactions of Organometallic Compounds in Benzene Solution. I. A. Korshunov and A. A. Orlova.	45	45
Radiochemical Determination of the Number of Carbon Atoms in an Organic Molecule. I. A. Korshunov and N. F. Novotorov	48	47
The Problem of the Dissociation of Arylcarbinols and Some Other Compounds in Nitrobenzene. I. E. I. Kviat and O. F. Ginzburg	52	51
Investigations of Cyclic Arylazo-β-diketones. I. Condensation of 1,3-Indandiol with Diazo Compounds. Z. Iu. Gudrinietse and G. Ia. Vanag	59	58
Investigations on Imidazole Derivatives. XVIII. The Problem of the Nitration of 5-Methylbenzimidazole. L. S. Efros and A. V. El'tsov.	64	62
The Condensation of Methyl Esters of α-Amino-β-mercaptocarboxylic Acids with Bromopyruvic Acid. I. T. Strukov	71	69

CONTENTS (continued)

	PAGE	RUSS. PAGE
Investigations on Conjugated Systems. LXXXII. Infrared Spectra of Vinylacetylenic and Dienic Ethers. A. A. Petrov and G. I. Semenov.	73	71
Investigations on Quinones. XX. Preparation of Naphthoquinones and Dihydroanthraquinones. A. N. Grinev and A. P. Terent'ev	77	75
Investigations on Quinones. XXI. The Structure of Substances Prepared by Condensation of Toluquinone and α-Naphthoquinone with Ethyl Acetoacetate. A. N. Grinev and A. P. Terent'ev	80	78
The Mechanism of the Dehydration of γ-Glycols. V. Study of the Properties and Transformations of the Acetylenic γ-Glycol 3-Methyl-1-hexyn-3,6-diol. T. A. Favorskaia and O. V. Sergievskaia	88	87
Sulfonation of β-Diketones with Dioxane Sulfotrioxide. II. Indandione-1,3-sulfonic-2 Acid and Its Salts. E. Iu. Gudrinietse, A. F. Ievin'sh and G. Ia. Vanag	95	95
Reaction of Hydrogen Peroxide with Allyl Alcohol and Acrolein in the Presence of Tungstic Acid. P. G. Sergeev and L. M. Bukreeva	101	101
Synthesis of Quinuclidine-3-Acetic Acid. E. E. Mikhlina and M. V. Rubtsov	104	103
Hydrogenation in the Presence of Colloidal Palladium. IX. Hydrogenation of Vinylpropyl- and Vinylbutylacetylenes. Kh. V. Bal'ian, Z. A. Lerman and L. A. Merkur'eva	110	110
Synthesis of 6-Methyloctene-1-yne-4-diol-3,6 and 7-Methyloctene-2-yne-5-diol-4,7 and Their Catalytic Hydrogenation. A. I. Nogaideli, K. Ia. Dzagnidze and R. Papava	116	116
Investigation of Lignin in Husks of Cotton Seeds. A. F. Semechkina and N. N. Shorygina	119	119
Synthetic Anesthetics. XXII. Phenoxyacetates of 1-Phenyl-3-dimethylaminopro-an-1-pan-1-ols. I. N. Nazarov and E. M. Cherkasova	122	122
Synthetic Anesthetics. XXIII. Phenoxyacetates of 1-Phenyl-2-methyl-3-dialkylaminopropan-1-ols. I. N. Nazarov, E. M. Cherkasova and Ch'ang Ch'ung Kwang	127	126
Oxidation of Organic Compounds. XV. Vapor Phase Oxidation of Ethylbenzene on Tin Vanadate. A. V. Solomin, B. V. Suvorov and S. R. Rafikov	134	133
Synthesis, Properties and Polymerization of α-Chloroacrylamide. S. S. Ivanov and M. M. Koton	139	139
A Study of the Chemical Structure of the Spongy Divinyl Polymer. II. A. I. Iakubchik, A. I. Spasskova and V. A. Tsitokhtsev	143	143
Condensation of ω-Bromoacetophenone with Diethanolamine. B. M. Mikhailov and A. N. Makarova	149	150
Organic Insectofungicides. XXVIII. The Synthesis of Some Esters of Bicyclo-(2,2,1)-heptenyl-5-carbinol-2. S. S. Kukalenko and N. N. Mel'nikov	153	154
Organic Insectofungicides. XXIX. The Reaction of Hexachlorocyclopentadiene with Some Unsaturated Compounds. S. S. Kukalenko and N. N. Mel'nikov	157	157

CONTENTS (continued)

	PAGE	RUSS. PAGE
Tertiary Amines of Some Heterocyclics as Possible Hypotension Remedies. E. S. Nikitskaia, V. S. Usovskaia and M. V. Rubtsov	161	161
Synthesis of Racemic Methyl Ether of O,O-Dibenzylmagnoline. I. N. Gorbacheva, L. P. Varnakova, E. M. Kleiner, I. I. Chernova and N. A. Preobrazhenskii	167	167
Diene Hydrocarbons from Unsaturated Alcohols. I. Catalytic Dehydration of Crotyl Alcohol to Butadiene. Iu. A. Gorin, V. S. Ivanov, E. S. Bogdanova and E. A. Piaivinen	170	169
Reaction of Alkylene Sulfides with Halides of Carboxylic Acids. S. Z. Ivin	177	177
Reaction of Halides of Carboxylic Acids with Aliphatic α-Oxides. S. Z. Ivin	181	180
Sulfonation Reaction. XLVI. Equilibrium Between Toluenetrisulfonic Acid and Its Trichloride. A. A. Spryskov and Iu. L. Kuz'mina	185	184
Reaction of Some Organosilicon Compounds with Cellulose Nitrates. A. P. Kreshkov, I. Ia. Guretskii and P. A. Andreev	188	187
Derivatives of Alkylphosphonous and Phosphonic Acids. VIII. Synthesis and Properties of Some Alkylated Amides of Alkylphosphonic Chlorides. A. I. Razumov, O. A. Mukhacheva and E. A. Markovich	194	194
Some Aryl Derivatives of Cyanothiourea. V. L. Nirenburg, I. Ia. Postovskii and V. M. Cherkasov	198	198
Mechanism of the Reaction of Transamination in the β-Dialkylaminopropionitrile Series. A. F. Bekhli	204	204
On the Products of Reaction Between Methylene Bases of Benzothiazole and Benzselenazole and Alkyl Halides. F. S. Babichev and A. I. Kiprianov	209	209
Synthesis of Aliphatic Amino Acids from Thiophene Derivatives. II. Synthesis of β-Amino Acids. Ia. L. Gol'dfarb, B. P. Fabrichnyi and I. F. Shalavina	213	213
Synthesis of Pyrrolidine Bases from γ-Ketoalcohols. A. P. Terent'ev, M. A. Volodina and V. G. Mishina	222	223
Haloarylation of Unsaturated Compounds by Aromatic Diazo Compounds. X. Synthesis of DL-Phenylalanine and Its Homologs. A. M. Iurkevich, A. V. Dombrovskii, and A. P. Terent'ev	226	227
Substances Capable of Forming Complexes. I. Synthesis and Structure of "Complexon -IV" – 1,2-Diaminocyclohexane-N,N,N',N'-tetraacetic Acid. V. G. Iashunskii and M. N. Shchukina	230	230
Methyl Linoleate Monoxide and Its Properties. G. V. Pigulevskii and I. N. Naidenova	234	234
Investigation of Aromatic Compounds with a Long Side Chain. II. Preparation of Dodecylaniline by Ammonolysis of p-Chlorododecylbenzene. L. N. Nikolenko and K. K. Babievskii	238	238
β-Acyloxyacroleins. T. V. Protopopova and A. P. Skoldinov	241	240
Auto-oxidation of a Methylene Group Bound to an Aromatic Nucleus. II. Auto-oxidation of the Methyl Ester of 9-Phenylundecanoic Acid. P. G. Sergeev and A. M. Sladkov	244	244

CONTENTS (continued)

	PAGE	RUSS. PAGE
Analogs of Steroid Hormones. I. Preparation of 3-(4-Oxocyclohexyl)-2-methylcyclopentanol. V. I. Maksimov and Z. A. Priakhina	247	246
Analogs of Steroid Hormones. II. Synthesis of 6-(2-Methyl-3-hydroxypentyl)-$\Delta^{1(9)}$-2-octalone. V. I. Maksimov and Z. A. Priakhina	253	253
Alkaloids of Salsola Richteri. VI. Structure of Salsamine. N. F. Proskurnina	257	256
Aconite Alkaloids. IX. Alkaloids of Aconitum excelsum. T. F. Platonova, A. D. Kuzovkov and P. S. Massagetov	259	258
Electrolytic Reduction of 2,4-Diamino-5-isonitroso-6-hydroxypyrimidine. V. M. Berezovskii and Iu. P. Sobolev	262	261
Determination of the Number of Electrons Participating in the Process for the Reduction of Stypticine at a Dropping Mercury Electrode. II. N. Ia. Khlopin and G. F. Reikhardt	266	264
The Preparation and Certain Properties of Silicon Nitride. V. F. Funke and G. V. Samsonov	269	267
The Electrolytic Reduction of Thorium Tetrachloride in Salt Melts. L. D. Iushina	274	272
Electrolytic Dissociation in Nonaqueous Systems. VI. System Allyl Mustard Oil—o-Toluidine. S. P. Miskidzh'ian	278	276

Letter to the Editor

Enthalpy of Formation of Nickel Carbonyl. B. F. Ormont and E. I. Smagina	281	279

JOURNAL OF GENERAL CHEMISTRY OF THE USSR

Volume 28, Number 2 February 1958

CONTENTS

	PAGE	RUSS. PAGE
A Study of Aqueous Solutions of Acetic Acid by the Method of Raman Spectra. A. A. Glagoleva and A. A. Ferkhmin	285	289
Ternary Reciprocal System of Sodium and Potassium Formates and Nitrates. O. I. Dmitrevskaia	295	299
Reduction of Nitrophenols at a Multidrop Mercury Cathode. L. N. Vertiulina and N. I. Maliugina	301	304
Polarographic Study of Aminoacetophenones. V. D. Besuglyi, V. N. Dmitrieva and V. V. Dorofeev	305	308
Synthesis of Vinyl Monomers. I. α-Substituted Derivatives of Vinylphosphonic Acid. A. Ia. Iakubovich, L. Z. Soborovskii, L. I. Muler and V. S. Faermark	313	317
Synthesis of Vinyl Monomers. II. Some Derivatives of α-Chrloroacrylic Acid. A. Ia. Iakubovich, E. P. Pravova and N. A. Bogoslovskii	316	320
Decarboxylation of Acridine-9-Carboxylic Acids With Carbonyl-containing Compounds. A. I. Gurevich	318	322
On the Products Formed in the Condensation of n-Butanol in the Presence of Sodium Butoxide and a Copper Catalyst. V. I. Liubomilov and E. T. Belianina	322	326
Reaction of Butyraldehyde with a Solution of Sodium Butoxide in n-Butanol. V. I. Liubomilov	324	328
Effect of Nucleophilicity of the Anion on the Character of Bonding in Compounds of Tropylium. M. E. Vol'pin, I. S. Akhrem and D. N. Kursanov	326	330
Simultaneous Hydrolysis of Mono- and Trifunctional Alkyl(aryl)chlorosilanes. K. A. Andrianov, M. Ia. Levshuk, S. A. Golubtsov and T. A. Krasovskaia	330	333
Synthesis and Properties of Tetrakis(tribenzylsiloxy)silane and Tetrakis(tribenzylsiloxy)methane. V. S. Chugunov	333	336
Trimethoxy- and Triaryloxyphosphazosulfonitrophenyls and Diesters of Nitrophenylsulfonamidophosphoric Acids. A. V. Kirsanov and N. G. Feshchenko	336	339
Substituted Imido- and Monoarylsulfamides. A. V. Kirsanov and Iu. M. Zolotov	340	343
Trichlorophosphazoaryloxydichloroacetyls. A. V. Kirsanov and V. P. Molosnova	344	347
Reaction of Tetrafluoroethylene with Arsenic Trichloride in the Presence of Aluminum Chloride. A. B. Bruker, T. G. Spiridonova and L. Z. Soborovskii	347	350

CONTENTS (continued)

	PAGE	RUSS. PAGE
Structure and Chemical Transformations of Alkali-organic Compounds of Anils. III. Transformations of Disodium and Dilithium Compounds of Benzophenone-o-Tolylimide and Benzophenone-p-Tolylimide under the Influence of Alkyl Halides. B. M. Mikhailov and K. N. Kurdiumova	352	355
Isoxazole Derivatives. V. Substitution in 5-Phenylisoxazole. N. K. Kochetkov and E. D. Khomutova	356	359
Reaction of Aromatic Compounds with Alcohols in the Presence of Acid Catalysts. III. Reaction of Phenol with Diols in the Presence of Phosphoric Acid. I. P. Losev and O. V. Smirnova	359	363
Chemistry of Naphthacene. VII. Nitration of Naphthacene. N. P. Bedniagina, G. A. Panfilov and I. Ia. Postovskii	361	365
Investigation in the Field of the Dieckmann Reaction. III. Cyclization of the Diethyl Ester of α-Methylpimelic Acid. N. S. Vul'fson and V. I. Zaretskii	365	369
Catalytic Conversions of Halogen Derivatives of the Aromatic Series. IV. A Study of the Mechanism of the Catalytic Isomerization of Monochloronaphthalenes Using Labeled Atoms. N. N. Vorozhtsov, Jr., and V. A. Koptiug	368	372
Investigations in the Field of 2,1,3-Thiodiazole Chemistry. VII. Thiocyanation of 4- and 5-Aminobenz-2,1,3-Thiodiazoles. V. G. Pesin and A. M. Khaletskii	378	383
Investigation in the Field of the Dieckmann Reaction. IV. Cyclization of the Tetraethyl Ester of 2-Methylpentanetetracarboxylic-1,1,5,5 Acid. V. I. Zaretskii and N. S. Vul'fson	382	388
Reactions of Metal Alcoholate Halides. V. The Mechanism of the Reaction of Magnesium Carbinolate Halides with Esters. I. I. Lapkin, O. M. Lapkina and M. N. Rybakova	385	391
Models of the Microstructures of Protein. III. The Structure of Phenylalanine Anhydride Derivatives. L.N. Akimova, I. P. Kuranova and N. I. Gavrilov	391	398
Preparation and Investigation of Some Properties of N-Monoaminoacyl Substituted Sarcosine Diketopiperazines. N. A. Poddubnaia and G. I. Lavrenova	396	404
Investigation of Pinacolin Isomerization Using Labeled Atoms. Z. N. Parnes, S. V. Vitt and D. N. Kursanov	402	410
Alkylation of Diphenyl With Alcohols in the Presence of $BF_3 \cdot H_3PO_4$ Catalyst. I. A. Romadan and S. E. Berga	405	413
Cases of Hindered Polymerization of Monomers in the Aryl Methacrylate Series. M. M. Koton, T. A. Sokolova, M. H. Savitskaia and T. M. Kiseleva	409	417
The Structure of the Potassium-Divinyl (Butadiene) Polymer. A. I. Iakubchik and N. N. Motovilova	413	421
Investigations on Conjugated Systems. LXXXIII. The Structure and Reactivity of the Methyl Ester of Vinylacetylene Carboxylic Acid. A. A. Petrov, K. B. Rall and G. I. Semenov	417	424
Oxidation of Vinylacetylenic Hydrocarbons by Organic Hydroperoxides. V. Oxidation of 6,9-Dimethyl-5,9-Tetradecadien-7-yne, 4,7-Dimethyl-3,7-Decadien-5-yne and 3,6-Diethyl-2,6-Octadien-4-yne by Acetyl Hydroperoxide. N. M. Malenok, S. D. Kul'kina and Z. Iu. Kovtunenko	421	428

CONTENTS (continued)

	PAGE	RUSS. PAGE
Oxidation of Vinylacetylenic Hydrocarbons by Organic Hydroperoxides. VI. Oxidation of 1-Phenyl-3-Methylocten-3-Yne-1 by Acetyl Hydroperoxide. N. M. Malenok and S. D. Kul'kina.	427	434
2-Phenyl-3-Bromobutene-2 in the Grignard Reaction. V. I. Pansevich-Koliada.	430	438
Investigations on Imidazole Derivatives. XIX. Amino Derivatives of Benzimidazolone and 1,3-Dimethylbenzimidazolone. L. S. Efros and A. V. El'tsov.	433	441
Investigations on Quinones. XXII. The Synthesis of Substituted Indoles. A. N. Grinev, I. A. Zaitsev, V. I. Shvedov and A. P. Terent'ev	439	447
Synthetic Analgesics. XXIV. Esters of 1-Phenyl-2,2-Dimethyl-3-Dialkylamino-propan-1-ols. I. N. Nazarov, E. M. Cherkasova and Chan Chon Khvan	443	452
Acetylene Derivatives. 190. Preparation of Ethoxyacetylene and its Employment for the Synthesis of Unsaturated Aldehydes and Acids. I. N. Nazarov, Zh. A. Krasnaia and V. P. Vinogradov.	451	460
Organic Insectofungicides. XXX. Synthesis of Some Derivatives of 1-Methylcyclopentane-dione-2,3. N. N. Mel'nikov and K. D. Shvetsova-Shilovskaia	464	474
Organic Insectofungicides. XXXI. A New Method of Preparing Mixed Esters of Thiophosphoric Acid. N. N. Mel'nikov, Ia. A. Mandel'baum and V. I. Lomakina	466	476
Organic Insectofungicides. XXXII. Synthesis of Some Mixed Esters of Thiophosphoric Acid. Ia. A. Mandel'baum, N. N. Mel'nikov and N. I. Petrova.	469	479
Organic Insectofungicides. XXXIII. The Synthesis of Some Derivatives of 4,7-Endomethyl-enetetrahydroindan. S. S. Kukalenko, N. N. Mel'nikov, T. I. Naryshkina.	471	480
Some Reactions of 2-Nitromethylquinoline. I. Salt Formation and the Action of Halogens. L. Zalukaev and E. Vanags	474	483
Vinylation of Hydrobenzoin. I. B. I. Mikhant'ev and L. P. Pavlov	478	487
A Study of the Effect of the Reagent's Character on the Direction of O- and C-Substitution of Metal Derivatives of a Keto-Enol System. V. A. Zagorevskii.	480	488
Some Esters of γ-Chlorocrotyl Alcohol. E. L. Gefter.	486	495
The Configuration and Properties of Unsaturated Acids and Their Derivatives. VIII. The Reactivity of Erucic and Brassidic Acids and Their Esters. A. K. Plisov and N. V. Bulatova	489	498
The Configuration and Properties of Unsaturated Acids and Their Derivatives. IX. The Properties of the α-Methylcrotonic Acids and Their Esters. A. K. Plisov and N. P. Paladienko	494	503
The Condensation of o-Aminothiophenols with Unsaturated Ketones and β-Haloketones. II. L. K. Mushkalo.	498	507
The Reactions of Hydrazine Derivatives. XVIII. The Action of Acidic Reagents on Azines. A. N. Kost, I. I. Grandberg and E. B. Evreinova	503	512
Derivatives of Hexamethylenimine. III. Substituted N-Benzylhexamethylenimines. G. S. Kolesnikov and L. I. Shcherbo.	509	519
Synthesis of Some Aminoalkyl Ethers with Cholinolytic Properties. S. G. Kuznetsov and Z. I. Bobysheva.	511	521

CONTENTS (continued)

	PAGE	RUSS. PAGE
Investigation of the Hydrogen Bond in Some Cholinolytic Substances Using Infrared Absorption Spectra. S. G. Kuznetsov and V. N. Nikitin	515	525
Investigations of the Synthesis of Steroid Hormone Analogs. III. Preparation of 3-(p-Methoxyphenyl)-Δ^2-Cyclopenten-1-One-2-Acetic Acid. G. S. Grinenko and V. I. Maksimov	519	528
Investigations in the Field of Analogs of Steroid Hormones. IV. Catalytic Hydrogenation of 3-(p-Methoxyphenyl)-Δ^2-Cyclopenten-1-One-2-Acetic Acid. G. S. Grinenko and V. I. Maksimov	522	532
Resin Acids. I. The Nature of α-Sapinic Acid. I. I. Bardyshev and V. V. Kokhomskaia	528	538
Resin Acids. II. The Nature of β-Sapinic Acid. I. I. Bardyshev and L. I. Ukhova	532	543
Investigations in the Field of Quinoline Derivatives XVII. Synthesis of some 6-and 8-Alkoxyquinolines. B. I. Ardashev and V. I. Minkin	535	545
Investigation of the Crystalline Substance Formed in the Production of Anabasine Sulfate. A. S. Labenskii	537	547
Steroid Sapogenins. III. The Sapogenins of the Rhizomes and Leaves of Yucca Filamentosa From the Black Sea Coast of Caucasia. O. S. Madaeva	541	551
Investigation of Aconite Alkaloids. X. Elatine. Structure of Esterifying Acid. A. D. Kuzovkov and A. V. Bocharnikova	546	556
Investigation of Aconite Alkaloids. XI. Oxidation of the Hydrocarbon $C_{18}H_{18}$, Formed During Dehydrogenation of Zongorine. A. D. Kuzovkov	549	558
A Discussion. In Reply to the "Remarks" by E. A. Shilov [1]. A. I. Titov and F. L. Makliaev.	551	561

JOURNAL OF GENERAL CHEMISTRY OF THE USSR

Volume 28, Number 3 March 1958

CONTENTS

	PAGE	RUSS. PAGE
Investigation of the Mechanism of Polycondensation of 1,3-Dichlorobutene-2 in the Presence of Friedel-Crafts-Gustavson Catalysts. I. A.L. Klebanskii, A.G. Saiadian and M.G. Barkhudarian.	555	569
Interaction of 1,3-Dichlorobutene-2 with Chloroprene under the Influence of Friedel-Crafts-Gustavson Catalysts. II. A.L. Klebanskii, A.G. Saiadian and M.G. Barkhudarian.	559	574
Investigation of the Exchange of Oxy-Radicals with Hydrocarbon Radicals of Organomagnesium Compounds. I. Investigation of the Reactivity of Mixed Acetals. M.F. Shostakovskii and M.R. Kulibekov	563	578
Electron Charge Density of Chemical Bonds and the Chemical Properties of Molecules. I. Energies of Activation of Substitution Reactions at a Saturated Carbon Atom. G.V. Bykov	568	584
Double Diazonium Salts of Methyltin Trichloride and Diethyltin Dichloride. O.A. Reutov, O.A. Ptitsyna and N.D. Patrina.	572	588
Investigation of Compounds Containing a Three-Membered Oxide Ring. XX. Reaction of Ethyl Esters of β-Nitrophenylglycidic Acids and p-Chlorophenylglycidic Acid with Ammonia and Aniline. V.F. Martynov and G. Ol'man.	576	592
Investigation of Compounds Containing a Three-Membered Oxide Ring. XXI. Reaction of Amides of β-Tetra- and β-Pentamethyleneglycidic Acids with Hexyl- and Benzylamines. V.F. Martynov and Zh.D. Vasiutina.	583	601
Reactions of Halometal Alcoholates. VI. A New Method of Synthesis of Monohydroxytriarylmethanes. I.I. Lapkin and M.I. Belonovich	586	605
Metalloorganic Synthesis of Dibiphenylalkanes and Diphenylalkanes. III. A.D. Petrov, E.P. Kaplan, Z.I. Letina and Iu.P. Egorov	589	608
Silicoalkylation of Aromatic Compounds by Dichloroalkylsilane Chlorides. E.A. Chernyshev, M.E. Dolgaia, Iu.P. Egorov, L.V. Semenov and A.D. Petrov.	593	613
Cyanoethylation of Benzimidazolone and Mercaptobenzimidazole. A.M. Efros	599	617
Chemistry of Selenophene. X. Synthesis of 3-Methylselenophene-2-aldehyde and 2,3- and 2,4-Dimethylselenophene. Iu.K. Iur'ev, N.K. Sadovaia and M.A. Gal'bershtam	602	620
Conversion of Allylbenzene Over Aluminosilicate Catalysts. I. Study of Conversion Kinetics. K.V. Topchieva, A.I. Pletiushkina and L.A. Zen'kovich	607	624
Conversion of Allylbenzene Over Aluminosilicate Catalysts. II. Structure and Mechanism of Formation of the Dimer. K.V. Topchieva, A.I. Pletiushkina and V.A. Tronova.	614	631

CONTENTS (continued)

	PAGE	RUSS. PAGE
Synthesis of Tagged Diethylaminoethyl S^{35}-Diphenylhydroxythioacetate. S.G. Kuznetsov, Z.I. Bobysheva, and E.M. Balonova	618	635
Investigations in the Field of Conjugated Systems LXXXIV: Dienyne Compounds. I. Synthesis and Properties of β-Alkoxydivinylacetylenes (Enol Ethers of Methylvinylethynyl Ketone). A.A. Petrov	621	638
Investigation of Ethers with a Double Bond in the Allyl Position. II. Synthesis of Ethers of α, α, γ, γ-Tetraalkyl-Substituted Allyl Alcohols. V.I. Pansevich-Koliada and I.F. Osipenko	624	641
New Synthesis of 2,6,10,14-Tetramethylhexadecen-15-ol-14, Isophytol. I.K. Sarycheva, G.A. Vorob'eva, N.A. Kuznetsova and N.A. Preobrazhenskii	630	647
Investigation of the Conversion of Pinacols with Substituted Acetylene Radicals. XV. Action of Mercuric Sulfate on Unsym. Dimethylphenyl(phenylethynyl)- and Unsym. Methyldiphenyl(phenylethynyl)Ethylene Glycols. L.A. Pavlova, A. Fabritsy and E.D. Venus-Danilova	634	651
Investigation in the Field of Vapor-Phase Catalytic Hydration of Acetylene and its Derivatives. I. Hydration of Vinylacetylene to Methylvinyl Ketone. Iu.A. Gorin and L.P. Bogdanova	640	657
On the Reaction of Ammonia with Methyl α-Chloroacrylate. S.S. Ivanov and M.M. Koton	644	661
Reaction of Dialkyl Phosphorous Acids with Aldehydes and Ketones. Esters of 1-Hydroxy-1-acetoethylphosphonic and 2-Hydroxy-4-keto-2-amylphosphonic Acids. V.S. Abramov, L.Sh. Belokon' and F.I. Makhmutova	647	665
Synthesis of 6-Carboxymethyl-1-azabicyclo[3.2.1]octane-7-carboxylic Acid and Some of its Derivatives. V.Ia. Furshtatova, E.E. Mikhlina and M.V. Rubtsov	650	668
Synthesis of γ-Amino Ketones. V.V. Perekalin and A.S. Sopova	656	675
Synthesis of Vinyl Monomers. III. Synthesis of Compounds with a Carbonyl Group. A.Ia. Iakubovich, V.V. Razumovskii and I.N. Beliaeva	660	680
Synthesis of Diureines of Some Nitrophenanthrenequinones. D.F. Kutepov, A.A. Potashnik and D.N. Khokhlov	663	682
Catalytic Polymerization of Polyphenyl- and Poly(dimethylphenyl)siloxanes. K. Andrianov, S. Dzhenchel'skaia and Iu. Petrashko	666	685
Some Derivatives of Mercaptocaffeine and Mercaptotheobromine. E.G. Berdichevskii, F.Iu. Rachinskii and E.K. Novoselova	670	689
Synthesis of Naphthalimide and its Derivatives. A.P. Karishin and D.M. Kustol	673	692
Preparation of Disubstituted Amidines from Disubstituted Thioureas and Methylmagnesium Iodide. N.V. Koshkin	676	695
Action of γ-Radiation of Radioactive Cobalt (Co^{60}) on Aqueous Solutions of Aromatic Hydrocarbons. M.A. Khenokh and E.M. Lapinskaia	679	698
Change in Proteins and Amino Acids under the Influence of Ultrasonic Vibrations. M.A. Khenokh and E.M. Lapinskaia	685	704
Reaction of Ketene with Nitrogen-Containing Bases. V. Acetylation of Bipiperidine with Ketene. Iu.V. Svetkin	692	711

CONTENTS (continued)

	PAGE	RUSS. PAGE
The Reaction of Ketene with Nitrogen-Containing Bases. VI. The Mechanism of the Acetylation of Amines with Ketene. Iu. V. Svetkin	694	713
A Study of the Comparative Reactivity of the Hydroxyl Groups in Cellulose. V. The Distribution of Methoxy Groups in Partly-Methylated Cellulose Obtained in an Alkaline Medium at Different Concentrations of Alkali. V. Derevitskaia, M. Prokof'eva and Z. Rogovin	697	716
A Study of the Comparative Reactivity of the Hydroxyl Groups in Cellulose. VI. The Distribution of Methoxy Groups in the Products of The Methylation of Na Cellulose Alcoholate. V. Derevitskaia, M. Prokof'eva and Z. Rogovin	700	718
The Kinetics of Oxidation of Cellulose by Nitrogen Peroxide According to Data Obtained from the Absorption Spectra of the Products. I.N. Ermolenko and M.M. Pavliuchenko	704	722
Synthesis of Heteroorganic Compounds of the Aliphatic Series by the Diazo Method. VIII. Synthesis of Compounds of Group V Elements. Organophosphorus Compounds. Experiments on the Synthesis of Di- and Trihaloalkylphosphines and Some Reactions of Chloroalkyl Derivatives of Phosphorus. V.A. Ginsburg and A.Ia. Iakubovich	710	728
Iodo Derivatives of Methylphosphine. V.A. Ginsburg and N.F. Privezentseva	716	736
Reactions of Magnesylamines. IV. Arylamidation of Aromatic Aldehydes with the Help of Arylamine-N,N-dimagnesium Halides. L.A. Tetiueva and P.A. Petiunin	719	739
Condensation of o-Aminothiophenols with β-Haloketones. Synthesis of Quaternary Salts in the Dihydrobenzohepta-1,5-thiazine Series III. L.K. Mushkalo	723	742
Reaction of Diazo Compounds with Sulfamic Acid and its Derivatives. VII. Reaction of Diazo Compounds with Unsubstituted Sulfamic Acid. D.Z. Zavel'skii and L.A. Lishnevskaia	726	745
Reactions of Diazo Compounds with Sulfamic Acid and its Derivatives. VIII. Diazonium Salts of Arylsulfamic Acids. D.Z. Zavel'skii and L.A. Lishnevskaia	735	755
Investigations on Thiosulfonic Acids. III. Alkyl Esters of Phenylmethane Thiosulfonic Acid and their Antibacterial Properties. B.G. Boldyrev and Iu.I. Kofman	746	768
The Reaction of Allyloxyethanol with Vinyl Ethers. V.N. Kotrelev and I.K. Rubtsova	748	770
The Synthesis of Phenyldifluoroacetic Acid and its Derivatives. L.M. Iagupol'skii and R.V. Belinskaia	750	772
Synthesis and Investigation of Poly-3, 3'-dimethyldiphenylmethaneadipo-N,N'-diethylamide. O.Ia. Fedotova, M.A. Askarov and L.N. Sedov	753	775
The Synthesis of N-Substituted Methacrylamides. IV. Acylation of Aromatic Amines with Methacrylyl Chloride in an Aqueous Medium. T.A Sokolova and L.A. Ovsiannikova	757	779
Sulfolysis of the Sulfonyl Groups in Aromatic Sulfonic Acids. F.M. Vainshtein and E.A. Shilov	760	782
Catalytic Reduction of Benzaldehyde. A.S. Sultanov, M.F. Abidova and V.A. Maslennikova	765	787
Investigation of Oxido Compounds. X. Reaction of α-Oxides of Allyl Ethers of Phenol, o- and p-Cresols and Guaiacol with Amines. Z.B. Idel'chik and V.I. Pansevich-Koliada	770	792

CONTENTS (continued)

	PAGE	RUSS. PAGE
The Number of Stable Oxides Formed by the Metals of the Long Periods of the Periodic System. S.A. Shchukarev.	773	795
Nuclear (Atomic) Concentration and Specific Gravities of Hydrocarbons. I.I. Zaslavskii . . .	788	811
The Viscosity of Binary Systems with Exchange Interaction. V.V. Udovenko and Iu.Ia. Fialkov	791	814
Physicochemical Analysis of Binary Systems Formed by Phenol with Acetic Acid and its Chloro Derivatives. I.M. Bokhovkin and E.G. Veselkova	795	819
Investigation of Continuous Transitions from Stable into Metastable Phase Separation. I.L. Krupatkin	800	823
Ternary Reciprocal System of Lithium and Sodium Formates and Nitrates. N.M. Tsindrik. . .	806	830
The Molecular Refraction of Certain Classes of Alkylthiophenes and Alkylthiacycloalkanes. P.G. Maslov and A.A. Klochikhin.	811	835
Discussion. Concerning the Papers of L.M. Litvinenko, R.S. Cheshko, S.V. Tsukerman, A.D. Gofman, B.M. Kolesnikova and Others on "Spatial Structure and Reactivity". E.N. Gur'ianova.	816	839

JOURNAL OF GENERAL CHEMISTRY OF THE USSR

Volume 28, Number 4 April 1958

CONTENTS

	PAGE	RUSS. PAGE
Basic and Acidic Oxides of Metals of the Large Periods of the Periodic System. S. A. Shchukarev	819	845
The Dissociation Constants of Trihydroxyglutaric Acid. N. K. Davidenko	832	859
Physicochemical Investigation of the Interaction of Acetone with Acetic Acid and Its Derivatives. I. M. Bokhovkin	835	862
Investigation of the Interaction of Diphenylamine with Organic Acids by the Methods of Physicochemical Analysis. N. K. Tsvetkova and D. E. Dionis'ev	840	868
Physicochemical Analysis of the System Ethylenediamine–Allyl Mustard Oil. M. P. Dianov and N. A. Trifonov	845	872
Ethylene Sulfide in the Synthesis of Heterocyclic Compounds with Two Hetero-Atoms. VII. 3-Arylthiazolidine-2-carboxylic Acids and Their Derivatives. Iu. K. Iur'ev and S. V. Diatlovitskaia	848	875
Reaction of 1,3-Dichlorobutene-2 with Isoprene and Divinyl Under the Influence of $FeCl_3$. III. A. L. Klebanskii, A. G. Saiadian, and M. G. Barkhudarian	853	881
1,4-Hydroxyketones and 1,4-Diketones in the Catalytic Synthesis of Homologs of Δ^2-Pyrroline and Δ^2-Dihydrothiophene, and, Correspondingly, Homologs of Pyrrole and Thiophene. Iu. K. Iur'ev and N. V. Makarov	857	885
Heterocyclic Derivatives of Methyl Ketones. F. N. Stepanov and S. L. Davydova	864	891
Synthesis and Reactions of Some Thiazolidine Derivatives. I. Preparation of Azorhodanines. A. P. Grishchuk and S. N. Baranov	869	896
Investigation of the Chemistry of Organic Oxides. XIV. Reaction of the α-Oxide of Isoprene with Ammonia and Amines. V. M. Al'bitskaia and A. A. Petrov	873	901
Investigation of Isomerization and Dimerization of Dimethylvinylcarbinol Relative to the pH of the Reagent. III. The Effect on Dimethylvinylcarbinol of Hydrochloric Acid, Saturated with Sodium and Magnesium Chlorides, and Hydrofluoric Acid. A. I. Lebedeva and L. F. Almashi	876	904
Investigation of Ethers with a Double Bond in the Allyl Position. III. Study of the Etherification of $\alpha,\alpha,\gamma,\gamma$-Tetraalkyl Substituted Allyl Alcohols. V. I. Pansevich-Koliada and I. F. Osipenko	881	909
Investigation of Oxido Compounds. XI. Reaction of α-Oxides of Allyl Ethers of Phenol, p-Cresol and Guaiacol with Methyl Alcohol. V. I. Pansevich-Koliada and Z. B. Idel'chik	887	914
The Abnormal Products of Vinyl-1-Cyclohexene-3 Ozonolysis. A. I. Iakubchik, A. I. Spasskova, and B. I. Tikhomirov	890	916

CONTENTS (continued)

	PAGE	RUSS. PAGE
Synthesis of Acetic Ester of Bis(Hydroxycyclohexyl)-1,3-butadiyne and Its Catalytic Hydrogenation. A. I. Nogaideli and G. M. Gonadze	895	921
Ethers of Glycols and Their Derivatives. XXXII. Synthesis of Monoethers of γ-Glycols and Their Alkoxymethyl Derivatives. Shamkhal Mamedov and A. F. Aliev	897	923
Diamines of Benzimidazole Series. I. Synthesis and Physicochemical Properties of Diamines. B. A. Porai-Koshits and Ch. Frankovskii	902	928
Diamines of Benzimidazole Series. II. Substantive Properties of the Azo Dyes Derived from the Diamines. B. A. Porai-Koshits and Ch. Frankovskii	908	934
Addition of Neutral Esters of Phosphorous and Phosphonous Acids to Conjugated Systems. IV. Addition of Esters of Phenylphosphonous Acid to α,β-Unsaturated Aldehydes and Acids. Gil'm Kamai and V. A. Kukhtin	913	939
Imidazole Derivatives. XX. Some Amino Derivatives of Benzimidazolone. L. S. Efros and A. V. El'tsov	916	941
Organomagnesium Synthesis and Properties of 1,1,1-Triphenylalkylmethanes, 1,5-Diphenyl-3-Benzylpentane, and 1-Phenyl-3-(2-Phenylethyl) Tridecane. II. M. A. Chel'tsova, A. D. Petrov, and Iu. P. Egorov	920	945
Reaction of Exchange of Hydroxyl Groups for Radicals of Organomagnesium Compounds. II. Reaction of Grignard Reagent with Symmetric Acetals. M. F. Shostakovskii and M. R. Kulibekov	926	951
Steric Hindrance in Organomagnesium Reactions. XVIII. Synthesis of Esters of α-(β-Alkoxy-1-naphthyl) Lactic Acids. I. I. Lapkin and V. Ia. Vlasova	930	955
Steric Hindrance in Organomagnesium Reactions. XIX. Synthesis of Esters of α-(4-Alkoxy-1-naphthyl) Lactic Acids. I. I. Lapkin and O. M. Lapkina	933	957
Heterocyclic Compounds. 61. Synthetic Analgesic Substances. XXV. Esters of 1,2,5-Trimethyl-4-phenyl (aryl)-4-piperidol. I. N. Nazarov, N. S. Prostakov, and N. N. Mikheeva	936	960
Synthesis of N-Methyl-3-carbomethoxy-4-hydroxypiperidines and a Study of Their Steric Structures. M. E. Maurit and N. A. Preobrazhenskii	943	968
Chemistry of Heterocycles. XXXII. Di- and Polyhalo Derivatives of 9-Phenylacridine with Positions of Halogen in Different Benzene Rings. M. E. Konshin and P. A. Petiunin .	949	974
Study of the Stephen Reaction. M. M. Shemiakin, V. I. Maimind, B. V. Tokarev, and V. I. Karpov	952	978
The Polymeric Peroxide of Vinyl Chloride. G. A. Razuvaev and K. S. Minsker	957	983
Reaction of Aromatic Compounds with Alcohols in the Presence of Acid Catalysts. IV. Reaction of Benzene with Polyhydric Alcohols in the Presence of Acid Catalysts. I. P. Losev and O. V. Smirnova	965	991
Reaction of Aromatic Compounds with Alcohols in the Presence of Acid Catalysts. V. Reaction of Benzene with Polyvinyl Alcohol in the Presence of Acid Catalysts. I. P. Losev and O. V. Smirnova	968	994

CONTENTS (continued)

	PAGE	RUSS. PAGE
Internal Complex Salts of Azo Compounds. V. Coppering of o-Hydroxy-o'-alkoxyazo Compounds with Simultaneous Dealkylation. V. I. Mur	972	998
Dipolar Ions, Formed by the Elimination of a Proton from an NH Group. XII. Derivatives of 6-Quinolinesulfonic Acid. A. M. Simonov	976	1003
Condensation of 6-Quinolinealdehyde with Ketones and Esters. B. P. Lugovkin	980	1007
Reaction of Diazo Compounds with Sulfamic Acid and Its Derivatives. IX. Reasons for the Color of Diazonium Salts of Arylsulfamic Acids. D. Z. Zavel'skii and L. A. Lishnevskaia	983	1010
Reaction of Hydrazine with Nitro Compounds of the Anthraquinone Series. II. Synthesis of Vat Dyes – Derivatives of Pyrazoleanthronecarboxylic Acid. N. S. Dokunikhin and I. D. Pletneva	991	1019
Azo Derivatives of Cyanine Dyes. A. I. Kiprianov and I. P. Fedorova	994	1023
The Reaction of Hydrazine with Carbon Disulfide Experiments on the Synthesis of Diisothiocyanogen. A. Ia. Iakubovich and V. A. Ginsburg	1002	1031
A Method of Obtaining Fluorine Derivatives of Silicon, Tin, and Sulfur. A. A. Iakubovich, S. P. Makarov, and V. A. Ginsburg	1006	1036
The Tautomerism of 9-Aminoacridine. A. K. Sukhomlinov	1009	1038
The Synthesis of 5,6,7-Trimethylisoalloxazines. V. M. Berezovskii and E. P. Rodionova	1016	1046
Esters of Aminophenylsulfonamidophosphoric Acid. A. V. Kirsanov and N. G. Feshchenko	1020	1049
Triaryloxyphosphazosulfonalkyls and Aromatic Esters of Alkyl Sulfonamidophosphoric Acids. A. V. Kirsanov and N. L. Egorova	1023	1052
Substances with Complex Forming Ability. II. Trans-1,2-diaminocyclopentane-N,N,N',N'-tetraacetic Acid and Trans-1,2-diaminocyclobutane-N,N,N',N'-tetraacetic Acid. V. G. Iashunskii	1026	1056
Cyanoethylation of Aryl Sulfonamides. A. E. Kretov and N. P. Romazanovich	1029	1059
Synthesis of the Diethyleneimide of 4-Methyluracil 5-Methylene Phosphinic Acid. A. Ia. Berlin and M. N. Vasil'eva	1033	1063
Studies in the Field of Synthesis and Polycondensation of N-Alkyl Derivatives of Hexamethylenediamine. I. Synthesis of N,N'-Dialkyl Derivatives of Hexamethylenediamine. D. L. Klebanskii and M. S. Vilesova	1036	1066
Research in the Field of Synthesis and Polycondensation of N-Alkyl Derivatives of Hexamethylenediamine. II. The Synthesis of N-Monoalkyl Derivatives of Hexamethylenediamine. A. L. Klebanskii and M. S. Vilesova	1042	1073
Synthesis of Alkoxy-Substituted Ketones of the Isoquinoline Series. L. I. Linevich	1045	1076
The Action of Nitrous Acid on Cyclic Salts of Salicylic Acid. The Preparation of 5-Diazosalicylic Acid. A. A. Nemodruk	1051	1082
Dimethyl Arylsulfon-N-methylamidophosphates. V. I. Shevchenko and G. I. Derkach	1054	1085
Alkaloids of Peganum Harmala L. II. The Structure of Two New Alkaloids. N. I. Koretskaia and L. M. Utkin	1056	1087

CONTENTS (continued)

	PAGE	RUSS. PAGE
Investigation in the Field of Indole Derivatives. V. The Problem of the Mechanism of the Fischer Reaction. N. N. Suvorov, N. P. Sorokina, and Iu. N. Sheinker	1058	1090
The Synthesis of Tropane-3-α-ol, Tropine. G. I. Bazilevskaia, D. V. Gura, M. S. Bainova, K. M. Diumaev, I. K. Sarycheva, and N. A. Preobrazhenskii	1065	1097
Reactions of Magnesylamines. V. The Mechanism of the Reaction of Aryl Amidation of Aromatic Aldehydes by N,N-Bis-(Magnesium halide)-Aryl Amines. P. A. Petiunin and L. A. Tetiueva	1072	1105
The Occurrence of Equilibrium of Three Liquid Phases in Ternary Systems. I. L. Krupatkin.	1075	1108
The Causes of the Transposition of Metals in the Electromotive Force Series in Fused Electrolytes. Iu. K. Delimarskii	1079	1112
In Memory of Andrei Ivanovich Lun'iak	1084	1118
Letter to the Editor. G. Chiurdoglu, Ch. Goldenberg, and J. Geeraerts	1086	1120

JOURNAL OF GENERAL CHEMISTRY OF THE USSR

Volume 28, Number 5 May 1958

CONTENTS

PAGE RUSS. PAGE

Studies in the Field of Conjugated Systems. LXXXV. The Condensation of Diene Halides with Acetylene Dicarboxylic Ester. V. S. Miklashevskaia and A. A. Petrov. 1187 1125

Studies in the Field of Conjugated Systems. LXXXVI. The Combination of Piperylene Hydrochloride with Isoprene. A. A. Petrov, N. A. Razumova and M. L. Genusov. 1190 1128

Acetylene Derivatives. 192. The Stereochemistry of Hydrogenation of Acetylenic Glycols. I. N. Nazarov, L. D. Bergel'son, L. P. Badenkova and B. V. Lopatin. 1195 1132

Investigation of the Vapor-Phase Catalytic Hydration of Acetylene and Its Derivatives. II. Hydration of Ethynylbenzene, Tert. Butylacetylene, Dimethylacetylene, Methylethylacetylene and Ethylvinylacetylene. Iu. A. Gorin and L. P. Bogdanova. 1205 1144

The Mechanism of the Catalytic Action of Aluminum Chloride. VI. More About the Kinetics and Mechanism of the Alkylation of Benzene with Chloro Derivatives. N. N. Lebedev . . 1211 1151

Stereochemical Investigations. III. Schiff Bases from Optically Active α-Phenylethylamine. A. P. Terent'ev and V. M. Potapov. 1220 1161

Preparation of α-Aminoacids Via Furan Derivatives. A. P. Terent'ev and R. A. Gracheva. . . . 1225 1167

Synthesis of 6,7-Disubstituted Derivatives of 1-Azabicyclo-(3.2.1)-Octane. V. Ia. Furshtatova, E. E. Mikhlina and M. V. Rubtsov. 1228 1170

Synthesis of Substituted Quinuclidine-2-Carbinols. L. N. Iakhontov, S. V. Iatsenko and M. V. Rubtsov. 1234 1177

The Synthesis of 1-Azabicyclo-[3.2.1]-Octane-7-Carboxylic Acid. A. K. Chizhov and M. V. Rubtsov. 1238 1181

Investigations in the Isoquinoline Series. XII. Synthesis of 4', 5'-Dimethoxy-5,6-Dimethyl-7-(1''-Methyl-6'',7''-Dimethoxy-1'',2'',3'',4''-Tetrahydroisoquinolyl)-3,4,5,6,7,8-Hexahydrobenzo[1',2':1,2]Quinolizine. R. P. Evstigneeva, N. M. Kashnikova, M. S. Bainova and N. A. Preobrazhenskii. 1241 1184

Investigations in the Isoquinoline Series. XIII. Synthesis of 8-Methylemetine. R. P. Evstigneeva, L. V. Lavrova, Ts. D. Zarankina and N. A. Preobrazhenskii. 1246 1190

Addition of Full Esters of Phosphorous and Phosphinous Acids to Conjugated Systems. V. The Problem of the Mechanism of the Reaction of Trialkyl Phosphites with Conjugated Systems. V. A. Kokhtin and Gil'm Kamai. 1252 1196

Iodonium Derivatives of β-Diketones. II. Thermal Decomposition of Phenyldimedonyliodone. O. Ia. Neiland, G. Ia. Vanag and E. Iu. Gudrinietse. 1256 1201

Synthesis of Thiazolidone Derivatives Having Biological Interest. VIII. Replacement of Some Radicals of Oxo-Compounds by Others in the Molecules of Derivatives of Thiazolidinedione-2,4-Hydrazone-2. N. M. Turkevich and E. V. Vladzimirskaia. 1260 1205

CONTENTS (continued)

	PAGE	RUSS. PAGE
A New Method of Synthesizing Esters of Phosphinic and Thiophosphinic Acids. XXIX. The Addition of Dialkyl Phosphorous Acids to Esters of Vinylacrylic and Sorbic Acids and 3,5 Heptadiene-2-One. A. N. Pudovik and I. V. Konovalova	1263	1208
An Investigation of the Thermal Decomposition of Etherates of Magnesium Iodide. I. On the Chemism of Oxonium Compounds. V. I. Esafov	1267	1212
An Investigation of the Thermal Decomposition of the Reaction Products of Dioxan with Magnesium Iodide Dietherate, Magnesium Iodide and a Mixture of Magnesium and Iodine. II. On the Chemism of Oxonium Compound. V. I. Esafov	1273	1218
The Synthesis and Investigation of the Chlorination Products of Acetylenyldivinyl (1,3-Hexadiene-5-Ine). A. N. Akopian, A. M. Saakian and M. G. Avetian	1276	1221
The Preparation and Properties of Some Aryl Derivatives of Thioxanthenol 5-Dioxide with Indicator Properties. V. S. Etlis and G. A. Razuvaev	1280	1225
Triaroxyphosphazoacyls. A. V. Kirsanov, G. I. Derkach and R. G. Makitra	1283	1227
Nitrogen Compounds of Phenylated Derivatives of Thiophene. I. V. N. Ivanova	1288	1232
The Absorption Spectra of α- and β-Phenylthiophenes and Their Nitro Derivatives. II. V. N. Ivanova	1293	1238
The Absorption Spectra and Structure of Substituted Quinolines Serving as Starting Substances for Antimalarials. V. Structure and Tautomerism of the 2- and 4-Aminoquinolines. V. I. Bliznìukov and N. T. Solonskaia	1295	1241
The Absorption Spectra and Structure of Acridine. V. I. Bliznìukov and A. K. Sukhomlinov	1301	1247
Relation Between the Acidity of Acyclic Polyols and the Length of the Polyhydroxylmethylene Chain. L. A. Mai	1304	1250
The Acidity of Some Monosubstituted Acetic Acids and the Electronic Affinity of Substituents. L. A. Mai	1306	1251
Synthesis and Transformations of Substituted Vinyl Ethers. VI. Synthesis of α-Methylvinylaryl and α-Methylvinylcyclohexyl Ethers. M. F. Shostakovskii, E. P. Gracheva and N. K. Kul'bovskaia	1308	1253
Interaction of Halides of Trivalent Iron with Nicotine. S. F. Babak and G. B. Kagramanova	1312	1257
Investigations on Amines and Quaternary Ammonium Compounds. X. Preparation of Isoprene from α,β- and γ,γ-Dimethylallyl Chlorides. A. T. Babaian, G. M. Mkrian and R. S. Giuli-Kevkhian	1314	1259
Substituted Hydrazides of Hydroxycarboxylic Acids. II. Synthesis of Arylhydrazides of Dialkylglycolic Acids. I. S. Berdinskii	1318	1263
Synthesis of Some Bifunctional Compounds Containing Sulfidic Sulfur. V. I. Lutkova and B. B. Berezina	1320	1265
Transformation Reactions of Methylolmethacrylamide. L. A. Arbuzova, S. N. Ushakov, S. A. Plotkina, V. N. Efremova and I. K. Ulezlo	1322	1266
Oxidation of α,β-Unsaturated Methyl Ketones with Sodium Hypobromite. N. E. Kologrivova and V. N. Belov	1325	1269

CONTENTS (continued)

	PAGE	RUSS. PAGE
Synthesis of Some Esters of 4,4'-Dihydroxydiphenyl Sulfone and Carboxylic Acids. S. N. Baranov, F. A. Zhoglo and R. V. Visgert	1330	1274
Cycloalkylation of Aromatic Compounds. XIV. Condensation of Cyclohexanol with Some Aromatic Hydrocarbons. N. G. Sidorova and I. A. Poliker	1333	1276
Synthesis of 1,4-Diisopropylbenzene and Some of its Transformations. S. V. Zavgorodnii, O. V. Sigov and I. F. Baev	1337	1279
Absorption Spectrum of 1,3-Cyclohexadiene in the 220-300 mμ Region. B. F. Erofeev, N. P. Emel'ianov and S. F. Naumova	1342	1284
Isotopic Exchange of Sulfur in Salts of Organic Thiosulfonic Acids. N. I. Grishko and E. N. Gur'ianova	1345	1287
Synthesis of Unsymmetrical Dialkylhydrazines. B. V. Ioffe	1354	1296
Tetraacyloxysilanes in Organic Synthesis. XIV. Synthesis of Homologs of Cinnamic Acid (α-Alkyl-β-Phenylacrylic Acids). Iu. K. Iur'ev, G. B. Eliakov and A. N. Vysokosov	1361	1302
Transamination Reactions of Carboxylic Acid Amides. N. V. Ridel' and M. P. Gerchuk	1365	1306
Mechanism of the Reduction of γ-Acetobutyronitrile. M. B. Braude	1368	1310
Research in the Field of Synthetic Dyestuffs. IX. Synthesis of Bisazo Dyes by the Condensation of Diazo Compounds with Salts of N-Aryl Quinaldines. G. T. Piliugin and S. V. Shinkorenko	1371	1313
Research in the Field of Synthetic Dyestuffs. X. Synthesis of N-Aryl-2-β-Anilinovinylquinoline Derivatives and Their Transformations. G. T. Piliugin, E. P. Opanasenko and S. V. Shinkorenko	1374	1316
Research in the Field of Synthetic Dyestuffs. XI. Condensation of Salts of N-Arylquinaldine with Nitroso Compounds. G. T. Piliugin and S. V. Shinkorenko	1378	1320
The Reduction of the Bisulfite Compound of 1-Naphthol. I. 1,2-Dihydrohaphthalene-2-Sulfonic Acid. S. V. Bogdanov	1382	1324
The Reduction of the Bisulfite Compound of 1-Naphthol and Its Oxime. II. S. V. Bogdanov	1386	1328
On the Synthesis of Choline and Thiocholine Esters of Carboxylic Acids. S. Z. Ivin	1390	1332
Reactions of Aromatic Nitro Compounds. III. A New Method for the Preparation of Alkyl Ethers of 2,4-Dinitrophenol. S. S. Gitis and A. J. Glaz	1393	1334
On the Liquid-Phase Catalytic Chlorination of Methylchlorosilanes. G. V. Motsarev, A. L. Englin, A. Ia. Iakubovich, I. N. Uspenskaia and N. G. Ivanova	1395	1336
Improved Methods of Synthesis of Phenyldichlorophosphine and Phenylphosphinic Dichloroanhydride. E. L. Gefter	1398	1338
The Structure and Transformations of Methylaryl-N-Nitrotriazenes. III. On Some Properties of Methylaryl-N-Nitrotriazenes. N. M. Baranchik, I. V. Grachev and D. Z. Zavel'skii	1400	1340
δ-Lactones. XII. Synthesis and Properties of 6-Phenyl-3,4-Dihydro-α-Pyrone. M. Iu. Lur'e, I. S. Trubnikov, N. P. Shusherina and R. Ia. Levina	1410	1351

CONTENTS (continued)

	PAGE	RUSS. PAGE
Preparation of Oxides of α,β-Unsaturated Higher Fatty Acids and Study of Their Properties. P. A. Artamonov	1414	1355
Substances Capable of Complex Formation. III. Cis-1,2-Diaminocyclohexane. V. G. Iashunskii	1420	1361
Research in the Field of Substituted Phenylosazones and Phenylhydrazones. II. Some New Nitrophenylosazones of Dihydroxytartaric Acid. N. V. Chugreeva	1424	1365
Investigation of the Relative Reactivity of the Hydroxyl Groups of Cellulose. VII. On the Distribution of Methoxyl Groups in Partially Methylated Cellulose, Obtained from Cellulose Treated with Sodium Isoamylate. V. Derevitskaia, M. Prokof'eva and Z. Rogovin	1427	1368
Thyroid Gland Hormones and Their Analogs. II. Synthesis of Isomers of Betazine. N. N. Suvorov and A. A. Dudinskaia	1430	1371
Thyroid Gland Hormones and Their Analogs. III. Synthesis of Amino Analogs of Betazine. N. N. Suvorov, A. A. Dudinskaia and L. M. Morozovskaia	1433	1374
N-Oxides of the Quinoxaline Series. II. N-Oxides of β-(Quinoxalyl-2)-Propionic and β-(Quinoxalyl-2)-Acrylic Acids. A. S. Elina	1437	1378
Cardiac Glycosides of the Seeds of Worm-Seed Mustard (Erysimum cheiranthoides L.). N. P. Maksiutina	1441	1383
Investigation of Complex-Formation in Solutions of Ternary Systems by Physicochemical Analysis Methods. IX. The Systems $AlBr_3-(iso-C_5H_{11})_2O-C_6H_5Br$ and $AlBr_3-(iso-C_5H_{11})_2O-C_6H_5Cl$. E. Ia. Gorenbein and V. N. Danilova	1445	1387
The Irreversible-Reciprocal System From Sodium and Potassium Formates and Thiocyanates. N. M. Sokolov and E. I. Pochtakova	1449	1391
The Irreversible-Reciprocal System From Sodium and Potassium Acetates and Propionates. N. M. Sokolov and E. I. Pochtakova	1455	1397
The Ternary System From Lithium and Sodium Propionates and Nitrates. N. M. Tsindrik and N. M. Sokolov	1462	1404
Complex Compounds of Stannic Chloride and Bromide with Urea. E. Sh. Iarmukhamedova and T. N. Sumarokova	1468	1410
Reduction of Limonene Monoxide with Lithium Aluminum Hydride. G. V. Pigulevskii, S. A. Kozhin and V. G. Kostenko	1471	1413
Academy of Sciences USSR Press "Akademkniga" Office. Books on Sale	1474	

JOURNAL OF GENERAL CHEMISTRY OF THE USSR

Volume 28, Number 6 June 1958

CONTENTS

	PAGE	RUSS. PAGE
Diene Hydrocarbons from Unsaturated Alcohols. II. Catalytic Dehydration of Tiglyl Alcohol and 2-Ethylhexen-2-ol-1 to Diene Hydrocarbons. Iu. A. Gorin, V. S. Ivanov and E. K. Khrennikova	1475	1421
Investigation of Conjugated Systems. LXXXVII. Addition of α-Chloro- and α-Bromo-Ether to Chloroprene. B. A. Vovsi and A. A. Petrov	1481	1426
Conjugated Systems. LXXXVIII. Condensation of 3-Chloro-1,3-pentadiene and 3-Chloro-1,3-hexadiene with Propargylaldehyde and Propiolic Acid. E. A. Leporskaia and A. A. Petrov	1486	1432
Conjugated Systems. LXXXIX. Influence of Various Factors on the Yield of Geranyl Chloride in the Reaction of Isoprene with Its Hydrochlorides. A. A. Petrov, Kh. V. Bal'ian, Iu. I. Kheruze, E. Iu. Shvarts, and L. L. Cherenkova	1490	1435
Acetylene Derivatives. 193. Total Synthesis of Isoprenoid Alcohols (Linalool, Geraniol, Nerol, Nerolidol, Farnesol, Geranyllinalool, Geranyl-Geraniol and Phytol). I. N. Nazarov, B. P. Gusev and V. I. Gunar	1498	1444
Simpler Analogs for Corticosteroids. I. Stereochemistry of Cyanohydrin and Acetylenic Synthesis. Configuration of 1-Cyano- and 1-Ethynyl-2-methylcyclo-hexanols. I. N. Nazarov, A. V. Kamernitskii and A. A. Akhrem	1511	1458
Investigations in the Field of Polymethylene Rings. XXX. Reaction of Diacetyl and Dibenzoyl with Dimethylhydrazine. N. A. Domnin, V. I. Diurnbaum, and V. A. Cherkasova	1520	1469
Investigation of Transformations of Pinacols with Substituted Acetylenic Radicals. XVI. Synthesis and Transformations of Sym. Dimethylphenyl(tertbutylethynyl) Ethylene Glycol (3,6,6-Trimethyl-2-phenylheptyn-4-diol-2,3). E. D. Venus-Danilova and V. I. Serkova	1528	1477
Investigations in the Pyrimidine Series. Action of Hydrogen Peroxide on Mercaptopyrimidines. Formation of Pyrimidine Sulfones and Their Instability in the Presence of Hydrogen Peroxide. Ch'ih Yueh-fon and Ch'en Shu-feng	1533	1483
Investigations in the Thiazole Series. V. Synthesis of 2-δ-Amino-n-butyl-4-N-diethylaminomethylthiazole. Ch'ih Yueh-fon and Zin Shih-yung	1542	1492
An Anomalous Reaction of α-Halo Ketones with Esters of Phosphorous Acid. VII. Reactions of Esters of Phosphorous Acid with Chlorinated Derivatives of β-Diketones. A. N. Pudovik and L. G. Biktimirova	1545	1496
The Problem of the Bromination of Cyclic Ketones with Dioxane Dibromide. L. V. Machinskaia and A. S. Podberezina	1550	1501

CONTENTS (continued)

	PAGE	RUSS. PAGE
5-Chlorofurylnitroolefins. Z. N. Nazarova and F. T. Pozharskii	1553	1503
Synthesis of Thiazolidone Derivatives of Biological Interest. IX. Synthesis of 3-Derivatives of 2,4-Thiazolidinedione Hydrazone. E. V. Vladzimirskaia	1555	1505
Interaction of β-Chlorovinyl Ketones with β-Dicarbonyl Compounds. V. Ketovinylation of α-Alkyl Acetoacetic Esters. N. K. Kochetkov, B. P. Gottikh and L. I. Kudriashov	1559	1508
Interaction of β-Chlorovinyl Ketone with β-Dicarbonyl Compounds. VI. Synthesis of some Derivatives of α-Pyrones. N. K. Kochetkov and L. I. Kudriashov	1562	1511
Synthesis and Properties of Pyrrolidine Bases. IV. 2-Methyl-N-β-aminoethylpyrrolidine and some of Its Transformations. A. P. Terent'ev, M. A. Volodina and V. G. Mishina.	1566	1516
4-Nitro-1,3-indanedione. G. Ia. Vanag and V. P. Oshkaia.	1570	1520
Synthesis and Polycondensation of N-Alkyl Derivatives of Hexamethylenediamine. III. Influence of the Structure of the Substituting Radical on the Direction of Alkylation of Hexamethylenediamine. A. L. Klebanskii and M. S. Vilesova.	1574	1524
Synthesis of N-Alkyl Derivatives of Hexamethylendiamine and Their Polycondensation. V. Some Problems of the Kinetics of the Reductive Alkylation of Hexamethylenediamine. A. L. Klebanskii and M. S. Vilesova	1578	1528
The Fermentative Synthesis of N-Peptides from O-Peptides of β-Hydroxyamino Acids. M. M. Botvinik and S. M. Avaeva	1583	1534
Investigation of the Exchange Reaction of Oxy Radicals with Radicals of Organomagnesium Compounds. III. Interaction of Organomagnesium Compounds with Mixed Organosilicon Acetals. M. F. Shostakovskii, M. R. Kulibekov, and I. A. Shikhiev.	1588	1539
Synthesis and Transformations of Butadienylsilanes. S. I. Sadykh-zade and A. D. Petrov	1591	1542
Reactions of Magnesylamines. VI. Steric Hindrance in the Aramidation of Aromatic Aldehydes with the Help of N,N'-bis-(halomagnesium)arylamines. P. A. Petiunin and L. A. Tetiueva	1596	1548
Synthesis of Organophosphorus Compounds from Hydrocarbons and Their Derivatives. VII. Oxidative Chlorophosphonation by Means of Alkyl and Dialkylamidophosphorodichloridites. Iu. M. Zinov'ev, V. N. Kulakova and L. Z. Soborovskii	1600	1551
Tetraacyloxysilanes in Organic Synthesis. XV. Synthesis of α,β-Unsaturated Acids of the Furan and Thiophene Series. Iu. K. Iur'ev, G. B. Eliakov and A. N. Vysokosov	1603	1554
The Chlorination of n-Hexane and n-Heptane. V. A. Nekrasova	1606	1557
The Problem of the Production of Aliphatic Alcohols from Petroleum Hydrocarbons. V. A. Nekrasova	1610	1561
Reaction of Dialkyl Dithiophosphates with Ethylene Sulfide. T. A. Mastriukova, V. N. Odnoralova and M. I. Kabachnik	1613	1563

CONTENTS (continued)

	PAGE	RUSS. PAGE
Organophosphorus Insecticides. Some Derivatives of Methylthiophosphonic and Methyldithiophosphonic Acids. M. I. Kabachnik, N. N. Godovikov, D. M. Paikin, M. P. Shabanova, N. M. Gamper and L. F. Efimova	1618	1568
An Investigation in the Field of Alkanesulfonic Acids. XVI. Chlorination of Anisidides of Alkanesulfonic Acids. A. G. Koštsova	1623	1573
Investigations in the Field of Quinoline Derivatives. XIX. A New Method of Synthesis of Quinolines by Rearrangement of Acylated Arylamines. B. I. Ardashev and V. I. Minkin	1627	1578
Interaction of Aqueous Solutions of Salts of Tetravalent Titanium with Pyrazolone Derivatives. R. G. Beiles	1631	1581
Anilides of Alkylsulfonamidophosphoric Acids. A. V. Kirsanov and N. L. Egorova	1636	1587
Salts of the Acid Fluorides of Arylsulfonamidophosphoric Acids. A. V. Kirsanov and E. S. Levchenko	1639	1589
Diphenylamides of Trichlorophosphazocarbonic Acids and Their Derivatives. A. V. Kirsanov and Z. D. Nekrasova	1644	1595
2,4-Di-(ethyleneimino)-1,3,5-triazines. L. E. Sventsitskaia, A. A. Kropacheva and S. I. Sergievskaia	1650	1601
Synthesis of p-Nitrophenylhalogenomethyl Carbinols. L. M. Iagupol'skii, B. E. Gruz and A. I. Kiprianov	1656	1608
Absorption spectra and Structure of the Bisulfite Compound of Acridine. V. I. Blizniukov and A. K. Sukhomlinov	1659	1610
Absorption Spectra and Structure of 2-Methoxyaminoacridine-9. V. I. Blizniukov and A. K. Sukhomlinov	1662	1613
Synthesis of Phosphoramidopyrimidines. Iu. P. Shvachkin and M. A. Prokof'ev	1665	1617
Chloromethylation of Saturated α,ω-Phenylaliphatic Acids. M. N. Bogdanov	1670	1621
Organozinc Compounds as Catalysts in the Polymerization of Propylene. G. A. Razuvaev, L. M. Bobinova, and V. S. Emlis	1672	1623
Condensation of Diacetone Alcohol with Benzene. I. P. Labynskii	1676	1626
Synthesis of Organophosphorus Compounds from Hydrocarbons and Their Derivatives. VIII. A Study of Oxidation of Phosphorus Trichloride by Oxygen. M. K. Baranaev, Iu. M. Zinov'ev, T. K. Skripach and L. Z. Soborovskii	1678	1628
Reactions of Free Radicals in Solution. XIV. Formation of Free Radicals in Decomposition of Hydrogen Disulfide and Their Reactions with α- and β-Olefins. E. I. Tiniakova, E. K. Khrennikova and B. A. Dolgoplosk	1682	1632
Orientation in Aromatic Ring Substitution. III. Isomerization of Dichlorobenzenes. A. A. Spryskov and Iu. G. Erykalov	1688	1637
The Study of Sulfonation Reaction. XLVII. The Study of Chlorobenzenesulfonic Acid Hydrolysis with the Use of Radioactive Indicators. A. A. Spryskov and O. I. Kachurin	1693	1642

CONTENTS (continued)

	PAGE	RUSS. PAGE
Mechanism of α-Tetraloxime Conversion into α-Naphthylamine. N. N. Vorozhtsov and V. A. Koptiug	1697	1646
The Problem of the Reduction of 1-Methyl-1-cyclohexene Oxide. G. V. Pigulevskii, S. A. Kozhin, and V. G. Kostenko	1706	1656
The Formation of 5-Benzylhydantoin-3-acetylvaline from the Methyl Ester of N-Carbobenzoxyphenylalanylglycylvaline. E. A. Morozova and S. M. Zhenodarova	1708	1658
The Synthesis of Cyanomethyl Esters of Peptides and Their Use in Obtaining Peptides. E. A. Morozova and S. M. Zhenodarova	1711	1661
Studies in the Field of the Chemistry of the Cyanine Dyes. XIII. Thiacyanines which Contain Unsaturated Radicals as Substituents in the 6,6'-Positions of Benzthiazole L. K. Ushenko and S. E. Gornostaeva	1717	1668
Monoanils of Glutaconic Aldehyde. I. Derivatives of Primary Aromatic Amines. N. E. Grigor'eva and A. A. Pechka	1726	1677
Monoanils of Glutaconic Aldehyde. II. Effect of the Medium on the Color of Derivatives of Primary Aromatic Amines. N. E. Grigor'eva and I. K. Gintse	1730	1682
Investigation of Anode Deposits Formed in the Electrolysis of Solutions of Certain Thallium Salts. III. M. S. Skanavi-Grigor'eva and V. I. Staroverova	1737	1689
Irreversible-Common System of Sodium and Potassium Butyrates and Thiocyanates. N. M. Sokolov and E. I. Pochtakova	1741	1693
Toward the Question of Contact Fusion of Crystals. P. A. Savintsev and V. E. Avericheva	1748	1700
Investigation of the Reaction of Phenyl- β-naphthylamine with Organic Acids by the Methods of Physicochemical Analysis. N. K. Tsvetkova and D. E. Dionis'ev	1750	1702
Compounds of Cadmium and Mercury Halides with Nicotine. I. A. Kondrashov and S. F. Babak	1753	1705

Letters to the Editor

Study of the Wallach Rearrangement and Related Reactions. M. M. Shemiakin, V. I. Maimind and B. K. Vaichunaite	1756	1708
Synthesis of L-Acetylalanine from D,L-Alanine. V. P. Spirichev and L. A. Shchukina	1758	1709

JOURNAL OF GENERAL CHEMISTRY OF THE USSR

Volume 28, Number 7 July 1958

CONTENTS

	PAGE	RUSS. PAGE
A Comparison of the Rate of Hydrogen Exchange With Protophilic Solvents. A. I. Shatenshtein and E. A. Iakovleva	1761	1713
Studies of the Reactions of Titanium Tetrachloride With Esters of Monobasic Acids. XII. The Decomposition of the Compounds $TiCl_4 \cdot$Ester. Iu. A. Lysenko and O. A. Osipov	1771	1724
Ternary Conjugate System of Lithium and Sodium Butyrates and Nitrates. N. M. Tsindrik and N. M. Sokolov	1775	1728
New Regularities in the Physicochemical Properties of Hydrocarbons. II. V. M. Tatevskii and V. A. Benderskii	1781	1733
Reactions of Polyhalogen Compounds With Alcohols. N. S. Vasileiskaya	1786	1738
Utilization of Benzene as a Solvent in Acetylation Reaction According to Friedel-Crafts. A. M. Sladkov	1791	1742
Accelerating Effect of Amines on Isotope Exchange of Sulfur in Organic Polysulfides. E. N. Gur'ianova and L. A. Egorova	1794	1745
Synthesis of 2-Ethylanthrone and 2-Ethyl-10-oxanthrone Labeled With Carbon C^{14} in the Nucleus and a Study of Some of Their Properties. S. V. Siavtsillo, V. I. Savushkina and E. M. Zhernovskaia	1800	1752
Tetraacyloxysilanes in Organic Synthesis. XVI. Benzoyloxytrichlorosilane and Reactivity of Benzoyloxy Group. Iu. K. Iur'ev and Z. V. Beliakova	1803	1755
Synthesis of Undecyl and Dodecylbenzenes and Their Perhydrides. A. D. Petrov, G. I. Nikishin and V. D. Vorob'ev	1809	1761
Research in the Field of Synthesis and Condensation of N-Alkyl Derivatives of Hexamethylenediamine. V. Reaction Mechanism of Reductive Alkylation of Hexamethylenediamine. A. L. Klebanskii and M. S. Vilesova	1815	1767
Research in the Field of Synthesis and Condensation of N-Alkyl Derivatives of Hexamethylenediamine. VI. Synthesis of Polyamides Starting With N-Alkylated Hexamethylenediamine. Production of Partly N-Alkylated Polyamides. A. L. Klebanskii and M. S. Vilesova	1820	1772
A Study in the Field of Synthesis of N-Alkyl Derivatives of Hexamethylenediamine and Their Polycondensation. VII. Preparation of Completely N-Alkylated Polyamides and Coupling of Their Chains With a Diisocyanate. A. L. Klebanskii and M. S. Vilesova	1824	1777

CONTENTS (continued)

	PAGE	RUSS. PAGE
Synthesis of 2-Ethyl- and 2-Propyl-1,3-butadienes. I. M. Dolgopol'skii, A. V. Tumanova, I. M. Dobromil'skaia and M. F. Egudina	1829	1782
Homologs of Monovinylacetylene. VII. Dehydration of Secondary Acetylenic Alcohols. I. A. Favorskaia, E. M. Auvinen and Iu. P. Artsybashev	1832	1785
The Simplest Analogs of Corticosteroids. II. Introduction of Dihydroxycarboxylic, Glyceryl and Hydroxylacetone Side Chains into o-Methylcyclohexanone and the Stereochemistry of the Compounds Formed Thereby. I. N. Nazarov and A. A. Akhrem	1837	1791
A Study in the Field of Stereochemistry of Cyclic Compounds. 28. Steric Directivity of the Serini Reaction in the Cyclohexane Series. I. N. Nazarov, A. A. Akhrem and A. V. Kamernitskii	1850	1805
The Synthesis of Mercaptoamino Compounds. III. Synthesis of 3-Mercapto-4-amino-2-methylbutane and 5-Amino-1-mercaptopentane. Iu. V. Markova, L. N. Zenkova and M. N. Shchukina	1856	1811
The Reaction of Dinitrodiolefins With Compounds Which Contain Mobile Hydrogen in Methylene Groups. V. V. Perekalin and O. M. Lerner	1861	1815
A Study of Iono-Catalytic Telomerization. I. Telomerization of Isoprene With Its Hydrochloride. K. V. Leets	1868	1823
The Chlorination of Ethylene Glycol. I. F. Spasskaia, V. S. Etlis and G. A. Razuvaev	1872	1827
Studies in The Field of Glycol Ethers and Their Derivatives. XXXIII. Some Chemical Transformations of γ-Bromoethers of the Aliphatic Series. Shamkhal Mamedov and B. K. Zeinalov	1876	1831
Studies in the Field of Glycol Ethers And Their Derivatives. XXXIV. Chemical Transformations of γ-Chloroethers, Shamkhal Mamedov and B. Pishnamazzade	1879	1834
N-Di(chloroethyl)amines of the Alicyclic Series. I. S. I. Sergievskaia, K. V. Levshina, A. K. Chizhov, A. I. Gavrilova and A. I. Kravchenko	1884	1839
N-Di(chloroethyl)amines With Alicyclic and Aromatic Radicals in the Molecule. II. S. I. Sergievskaia, K. V. Levshina, A. I. Gavrilova and A. K. Chizhov.	1890	1845
The Alkylation of Substituted 5-Hydroxybenzofurans; Synthesis of New Plant Growth Stimulants. A. N. Grinev, N. K. Venevtseva and A. P. Terent'ev	1894	1850
A New Method for Obtaining Substituted Benzofurans and Indoles From Esters of Benzofuran— and Indole-β-carboxylic Acids. A. N. Grinev, I. A. Zaitsev, N. K. Venevtseva and A. P. Terent'ev	1897	1853
Studies in the Field of Quinones. XXIII. Studies of the Condensation of p-Benzoquinone and 2,3-Dichloroquinone with Acetoacetic Ester and Its Analogs. A. N. Grinev, N. K. Venevtseva and A. P. Terent'ev	1900	1856
The Reaction of Ketene with Nitrogen-Containing Bases. VII. Chloroacetylation of Primary Amines. Iu. V. Svetkin and G. Kretsu.	1907	1864
Studies of Organic Sulfur Compounds. I. The Synthesis of Alkanesulfonyl Fluorides and Their Halogen Derivatives. L. Z. Soborovskii, B. M. Gladshtein, M. I. Kiseleva and V. N. Chernetskii	1909	1866

CONTENTS (continued)

	PAGE	RUSS. PAGE
Studies of Organic Sulfur Compounds. II. The Synthesis of Alkenesulfonyl Fluorides and Their Halogen Derivatives. L. Z. Soborovskii, B. M. Gladshtein, V. N. Chernetskii and M. I. Kiseleva	1913	1870
The Hydrolysis of Esters of Aromatic Sulfonic Acids. V. The Hydrolysis of Esters of Benzenesulfonic Acid and Substituted Phenols. R. V. Vizgert	1917	1873
Studies in the Field of Alkoxysilanes. XI. Reaction of Dialkyldiacetoxysilanes With Glycerol and Pentaerythritol. V. P. Davydova and M. G. Voronkov	1922	1879
The Splitting of Macrotominic Acid and Acids From Heliosupine in Caustic Alkali Solutions. S. I. Denisova, M. F. Petrova and G. P. Men'shikov.	1925	1882
Intermediate Products in the Condensation Reaction of Isoamyl Alcohol. V. I. Liubomilov and A. I. Kutsenko	1928	1885
Trichloroisophosphazoacyls of the Aromatic Series. A. V. Kirsanov and G. I. Derkach	1930	1887
Bis-Triaryloxyphosphazo-Sulfones and Tetraaryl Esters of Sulfamidobisphosphoric Acid. A. V. Kirsanov and L. L. Matveenko	1935	1892
Chemical Structure and Parasitocidal Activity. XXI. Concerning the Problem of the Connection of the Structural Stability of Derivatives of 9-Aminoacridine and Their Antimalarial Action. A. F. Bekhli	1943	1901
Chemical Structure and Parasitocidal Activity. XXII. Concerning the Problem of the Connection Between the Structure and the Antimalarial Action of Isomeric Chloro-4-aminoquinolines. A. F. Bekhli	1946	1904
An Improved Method of Synthesis of Di-β,β'-Chloroethyl Ester of β-Chloroethylphosphonic Acid. E. L. Gefter	1949	1908
A Study in the Field of the Dieckmann Reaction. V. Cyclization of Diethyl Ester of α-Carbethoxypimelic Acid. N. S. Vul'fson and V. I. Zaretskii.	1951	1909
Replacement of Halogen in Azo Compounds. I. Replacement of Chlorine in 2-Chlorophenylazo-2'-naphthol by Alkoxy Groups. B. I. Stepanov, M. A. Salivon, V. F. Lagidze and L. A. Dediukhina	1956	1915
Replacement of Halogen in Azo Compounds. II. Reaction of 2-Chlorophenylazo-2'-naphthol With Phenolates. B. I. Stepanov, L. A. Dediukhina and T. T. Strashnova. . .	1962	1921
Reaction of Diazo Compounds With Sulfamic Acid and Its Derivatives. X. Concerning Colored Salts of Acylaminoarylsulfonic Acids With Diazonium Bases. D. Z. Zavel'skii and L. A. Lishnevskaia	1966	1925
Syntheses of Vinyl Monomers. III. Concerning the Syntheses of Vinyl Esters From Aceto- and Chloromercuriacetaldehydes and Concerning the Mechanism of These Reactions. A. Ia. Iakubovich, V. V. Razumovskii, Z. N. Vostrukhina and S. M. Rozenshtein	1971	1930
A Study in the Isoxazole Series. VI. Concerning the Synthesis of 3-Substituted Isoxazoles. N. K. Kochetkov and A. Ia. Khorlin	1977	1937
A Study in the Field of Thiosulfonic Acids. IV. Concerning The Mechanism of the Reaction of Formation of Thiosulfonates. B. G. Boldyrev and T. A. Trofimova	1981	1940

CONTENTS (continued)

	PAGE	RUSS. PAGE
A Study of the Mechanism of Diazoexchange in Azo Dyes of the Naphthalene Series Made by Means of the Heavy Nitrogen Isotope. B. A. Geller	1985	1944
Reaction of N,N-Dichlorobenzenesulfonamide With Polyhalogen Derivatives of Methane. I. A. E. Kretov and M. M. Kremlev	1991	1950
Reaction of N,N-Dichlorobenzenesulfonamide With Polyhalogen Derivatives of Methane. II. A. E. Kretov and M. M. Kremlev	1995	1954
Thermocatalytic Transformations of α-Terpinene Over Gumbrin. V. V. Tishchenko and N. S. Lishenkova	1999	1957
The Complex – Pyridine-Cupreous Chloride – As An Autoxidation Catalyst. I. Preparation of Azo Compounds From Primary Aromatic Amines. A. P. Terent'ev and Ia. D. Mogilianskii	2002	1959
Indole Derivatives. V. Synthesis of Bis-Quaternary Ammonium Salts of Harmine. N. F. Kucherov, V. P. Evdakov and N. K. Kochetkov	2005	1962
β-Aminovinyl Ketones. IX. Salts of Trialkyl-(γ-oxoalkenyl)-ammonium As Oxovinylating Agents. L. I. Kudriashov and N. K. Kochetkov	2009	1967
Synthesis of Theophylline and Caffeine From Urea and Sodium Cyanoacetate. V. I. Khmelevskii and E. I. Abramova	2012	1970
Preparation of Theophylline and Caffeine From Uric Acid. V. I. Khmelevskii, E. I. Abramova and L. V. Variukhina	2016	1974
A Study in the Field of Polycyclic Quinones. III. Reaction of 1-Haloanthraquinone with Secondary Alkaromatic Amines. N. S. Dokunikhin and T. N. Kurdiumova	2021	1979
Steroids. I. Preparation of 21-Bromopregnanol-17α-Trione-3,11,20 From Pregnanol-3β-dione-11,20. O. K. Nikiforova and N. N. Suvorov	2025	1984
Steroidal Sapogenins. IV. A New Sarsaponine Isolated From Roots of Yucca Filamentosa. O. S. Madaeva	2029	1988
Steroidal Sapogenines. V. Sapogenines of Leaves of Agave Americana L. N. A. Serova and O. S. Madaeva	2032	1991
Effect of Substituents in the Molecules of Inhibitors on Their Protective Properties in Autoxidation of α-Pinene. E. N. Novikova	2035	1993

Letters to the Editor

	PAGE	RUSS. PAGE
About Properties of Polyamides With Siloxane Groupings. V. V. Korshak, P. M. Frunze, D. N. Andreev and E. V. Kukharskaia	2039	1997
The Problem of Thermodynamic Study of Lower Chlorides of Wolfram (Tungsten). S. A. Shchukarev, G. I. Novikov and N. V. Andreeva	2040	1998
Concerning the Order of Addition of Water and Alcohols to Vinylalkylacetylenes. A. A. Petrov and B. S. Kupin	2041	1999

JOURNAL OF GENERAL CHEMISTRY OF THE USSR

Volume 28, Number 8 August 1958

CONTENTS

PAGE RUSS. PAGE

Synthesis of Lead Tetraacetate by Electrochemical Oxidation of Lead Diacetate at the Anode. M.Ia. Fioshin and L.I. Kazakova 2043 2005

Ternary Reciprocal System of the Butyrates and Nitrates of Sodium and Potassium. O.I. Dmitrevskaia 2046 2007

The Reaction Between Sodium Tungstates and Stilbene-4,4'-bis-[(azo-1)-3,4-dihydroxybenzene]-2,2'-disulfonic Acid ("Stilbazo") in Aqueous Solutions. K.E. Kleiner and A.Kh. Klibus 2052 2013

Polarographic Investigation of p-Nitrosodimethylaniline. V.N. Dmitrieva and V.D. Bezuglyi 2059 2021

The Polarographic Determination of Some Derivatives of 2-Ethylanthraquinone. L.M. Shtifman, S.V. Siavtsillo and L.G. Kuriakova. 2066 2028

Cycloalkylated Aromatic Compounds XV. The Condensation of Fluorene with Cyclohexanol in the Presence of Aluminum Chloride. N.G. Sidorova and G.Kh. Tyshchuk. 2069 2030

Radical and Ionic Alkylation of the Aromatic Ring. VII. Butylation of Benzene, Naphthalene, Phenol and Anisole. S.G. Mel'kanovitskaia and I.P. Tsukervanik. 2071 2032

The Condensation of Benzotrichloride with Benzene in the Presence of Aluminum Chloride. I.P. Tsukervanik and Z.Ia. Belinson. 2077 2038

A Study of the Mobility of the Ethyl Group in Ethylbenzene and Its Derivatives by the Method of Isotope Exchange. L.M. Nazarova. 2082 2042

The Synthesis of Some Nitro- and Amino Derivatives of Tolan. L.M. Litvinenko, N.F. Levchenko and A.N. Androsov. 2086 2046

The Synthesis of Hydrocarbons. LXV. Di-tert-alkylmethanes from 2,4-Dimethyl-1,3-pentadiene. R.Ia. Levina, Iu.S. Shabarov and V.K. Daukshas. 2089 2049

A Study of the Chemical Structure of Sodium-Carbonic Acid Polymers of Divinyl. A.I. Iakubchik, A.I. Spasskova and L.A. Shibaev. 2095 2056

The Synthesis of Alkoxy Derivatives of Divinylacetylene. VII. The Direction of Addition of Ethyl Alcohol to Divinylacetylene. A.L. Klebanskii and D.M. Krasinskaia. 2100 2061

Studies in the Field of Polymethylene Rings. XXXI. The Reaction of 1-Chloro-1,2-dibromocyclohexane with Quinoline. N.A. Domnin and V.A. Cherkasova. 2103 2064

Studies in the Field of Sarcomycin and Its Analogs. II. Synthesis of Sarcomycin Isomers. M.M. Shemiakin, M.N. Kolosov, M.G. Karapetian and V.Ia. Rodionov. 2107 2068

Studies in the Field of Compounds Which Contain Three-Membered Oxygen Rings. XXII. The Reaction of Glycidic Acid Esters with α- and β-Naphthylamines. V.F. Martynov and N.P. Sukhinin 2113 2075

CONTENTS (continued)

	PAGE	RUSS. PAGE
Studies in the Field of Compounds Which Contain Three-Membered Oxygen Rings. XXIII. The Reaction of Ethyl Esters of β-Methyl-β-butyl- and β-Methyl-β-phenylglycidic Acids with Aniline. V.F. Martynov and Ia.A. Kastron	2119	2082
The Behavior of Some Dichloroalkanes and Dichloroalkenes in Conditions of Direct Synthesis. A.D. Petrov, G.I. Nikishin and N.P. Smetankina	2122	2085
Studies in the Field of the Chemistry of 2,1,3-Thiodiazole. VIII. The Oxidation of Benzo-2,1,3-thiodiazole and Its Derivatives. V.G. Pesin, A.M. Khaletskii and Chou Ch'in . .	2126	2089
Chemistry of 2,1,3-Thiadiazole. IX. Reaction of o-Benzoquinone Dioxime with Sulfur Dichloride. V.G. Pesin, A.M. Khaletskii and Chou Ch'in	2131	2094
Catalytic Preparation of Ketones from a Mixture of n-Butyric Acid and Ethyl Alcohol. G.V. Golodnikov, B.N. Dolgov and L.N. Propp.	2134	2097
Effect of Preliminary Thermal Destruction on the Oxidizability of Methane Hydrocarbons. V.G. Gavrilov and S.A. Velichko	2138	2100
The Problem of the Hydrogen Bond in Meconic Acid. M.I. Goriaev, V.S. Volkova and G.A. Tolstikov.	2140	2102
Organic Sulfur Compounds. III. Properties of Haloalkane-, Alkene- and Haloalkenesulfonyl Fluorides. B.M. Gladshtein, V.N. Chernetskii, M.I. Kiseleva and L.Z. Soborovskii. . .	2145	2107
Preparation of Organosilicon Hydroxy Compounds from Aminosilanes. I. Preparation of Alkylalkoxysilanes from Alkylphenylaminosilanes, Synthesized from Alkylchlorosilanes. A.P. Kreshkov, L.V. Myshliaeva and L.M. Khananashvili	2150	2112
Hydrolysis of Aromatic Sulfonic Acid Esters. VI. Alkaline and Aqueous Hydrolysis of Nitro-Substituted Aryl Sulfonates. R.V. Vizgert and E.K. Savchuk	2153	2114
Reactions of Aromatic Sulfonic Acid Esters. VII. Arylating Properties of Dinitrophenyl Benzenesulfonates. R.V. Vizgert and Ia.P. Berkman.	2158	2119
The Thermal Addition of Trichlorosilane to Diolefin Hydrocarbons. M.G. Voronkov and N.G. Romanova.	2161	2122
Investigations in the Field of Alkoxysilanes. XII. Hexa-tertiary-butoxycyclotrisiloxane. M.G. Voronkov, V.P. Davydova and A.N. Lazarev.	2167	2128
Investigations in the Field of Conjugated Systems. XC. The Addition of 2-Chloro-3-pentene to Divinyl. A.A. Petrov, N.A. Razumova and M.L. Genusov	2171	2132
Investigations in the Field of Conjugated Systems. XCI. The Addition of 1-Chloro-3-methyl-2-butene to Divinyl. A.A. Petrov and N.A. Razumova.	2178	2138
The Condensation of Diene Hydrocarbons with Cinnamaldehyde. The Synthesis of Hydroaromatic Alcohols, Acetates and Hydrocarbons. N.P. Sopov and M.L. Kovner	2184	2145
Synthesis of β-Chloro Substituted Alcohols and Their Conversions. M.L. Farberov and V.A. Speranskaia	2190	2151
The Chemistry of Selenophene. XI. α-Iodoselenophenes in the Organomagnesium Synthesis of Selenophene-α-carboxylic Acids. Iu.K. Iur'ev and N.K. Sadovaia	2200	2162
The Chemistry of Selenophene. XII. 5-Nitroselenophene-2-aldehyde and 5-Nitroselenophene-2-carboxylic Acid. Iu.K. Iur'ev and E.L. Zaitseva	2203	2164

CONTENTS (continued)

	PAGE	RUSS. PAGE
The Synthesis of 2,5-Dimethyl-3-alkylfuranidines. Iu.K. Iur'ev, E.G. Rozantsev and S.N. Godovikova	2207	2168
Some Amino Derivatives of Piazselenole. L.S. Efros and A.V. El'tsov	2211	2172
Investigation in the Field of Imidazole Derivatives. XXI. Synthesis and Properties of Imidazolobenzenes. L.S. Efros and A.V. El' tsov.	2214	2174
Investigation in the Field of the Synthesis of Steroid Hormone Analogs. V. The Synthesis of Some Compounds of the Cyclopentanotetrahydronaphthalene Series. V.I. Maksimov and G.S. Grinenko	2218	2179
Investigation in the Field of the Synthesis of Steroid Hormone Analogs. VI. Experiments on the Cyclization of Trans-3-(p-methoxyphenyl)-cyclopentano-1-one-2-acetic Acid and Its Derivatives. V.I. Maksimov and G.S. Grinenko	2222	2182
The Simplest Analogs of Corticosteroids. III. The Introduction of Dihydroxyacetone, Glycerol and Dihydroxypropanecarboxylic Acid Side Chains into Derivatives of Cis- and Trans-Decalins. I.N. Nazarov, G.V. Aleksandrova and A.A. Akhrem.	2227	2187
Synthesis and Transformations of Cis- and Trans-1-ethynyl-1-decalols. I.N. Nazarov, G.V. Aleksandrova and A.A. Akhrem	2237	2199
Investigation of Acridine Derivatives. 1. Synthesis of 1-Nitro-2-methoxy-9-chloroacridine. A.T. Troshchenko	2245	2207
Orientation in Substitution in the Aromatic Nucleus. IV. Sulfonation of Chlorobenzene. A.A. Spryskov and O.I. Kachurgin	2250	2213
The Study of Chitin. III. Hydroxyethyl and Ethyl Ethers of Chitin. S.N. Danilov and E.A. Plisko	2255	2217
Investigation in the Field of Compounds Labeled with C^{14} and N^{15}. IX. Synthesis of ω-N^{15}-Amino Acids. V.I. Maimind, O.M. Enisherlova, K.M. Ermolaev, R.G. Vdovina, G.A. Galegov and M.M. Shemiakin	2260	2223
Molecular Structure of Unsaturated Ketones – Bimolecular Cyclohexanone Condensation Products. Ts.N. Roginskaia, S.V. Svetozarskii, A.I. Finkel'shtein and E.N. Zil'berman	2266	2229
Reactions of Acyl Peroxides with Metals. G.A. Razuvaev and V.N. Lamiaeva	2270	2233
Synthesis of Some Isomeric Methoxy-Allyl-Diethylaminoethoxybenzenes. M. Pal'gi	2275	2239
Synthesis of β-Amino Acids from Aromatic Hydroxy and Alkoxyaldehydes. V.M. Rodionov, A.A. Dudinskaia, V.G. Avramenko and N.N. Suvorov.	2279	2242
Triaroxyisophosphazoacyls of Aromatic Series. A.V. Kirsanov and G.I. Derkach	2283	2247
Some β,β-Diarylethylamines. N.K. Kochetkov and M.I. Petruchenko.	2288	2252
Research in the Field of Unsymmetrical Organic α-Oxides. XVII. Reaction of Pentadienyl Oxide with Ethyl Sodioacetoacetate. F.G. Ponomarev and Iu.M. Mosichkin	2293	2257
Dissociation of Arylcarbinols and Some Other Compounds in Nitrobenzene. II. E.I. Kviat . .	2296	2260
Reactions of Aromatic Nitro Compounds. IV. Transalkylation of 2,4-Dinitrophenolic Ethers. S.S. Gitis, M.S. Malinovskii and A.I. Glaz	2299	2262
Addition of Hydrogen Halides to Esters of α,β-Unsaturated Acids. V.N. Mikhailova and V.V. Pigulevskii	2302	2265

CONTENTS (continued)

	PAGE	RUSS. PAGE
Preparation of ω-Hydroxypentadecanoic Acid by the Method of Electrolytic Cross Condensation. II. G.E. Svadkovskaia, E.K. Smol'ianinova and V.N. Belov	2305	2268
A Simplified Synthesis of 8-Mercaptoquinoline (Thiooxine) and Preparation of Its Potassium and Sodium Salts. Iu.A. Bankovskii, A.F. Ievin'sh and E.A. Luksha	2310	2273
Conversion of Δ^3-p-Menthene on Gumbrine. V.V. Tishchenko and V.F. Kazanskaia	2313	2277
A Study of Glucosides of Jute. I. Olitoriside. N.K. Abubakirov, V.A. Maslennikova and M.B. Gorovits	2316	2279
A Study of Aconite Alkaloids. XII. Structure of the Hydrocarbon $C_{18}H_{18}$ and the Possible Formula of Songorine. A.D. Kuzovkov	2320	2283
Syntheses of Vinyl Monomers. IV. Fluorine-Substituted Acrylates. A.Ia. Iakubovich, N.A. Bogoslovskii, E.P. Pravova and S.M. Rozenshtein	2325	2288
Syntheses of Vinyl Monomers. V. Syntheses of Cyano-Substituted Acrylates. A. Iakubovich, V. Razumovskii and S. Rozenshtein	2329	2292
Reaction of Nitrogen Tetroxide with Organic Compounds. I. A Study of Conditions of Reaction of Nitrogen Tetroxide with Benzaldoxime. Composition of Products and Reaction Equation. S.S. Novikov, L.I. Khmel'nitskii and O.V. Lebedev	2333	2296
Reaction of Nitrogen Tetroxide with Organic Compounds. II. Reaction of Nitrogen Tetroxide with aci-Phenylnitromethane and Its Salt. L.I. Khmel'nitskii, S.S. Novikov and O.V. Lebedev	2340	2303
Reaction of Nitrogen Tetroxide with Organic Compounds. III. Reaction of Nitrogen Tetroxide with Salts of Aliphatic Nitro Compounds. S.S. Novikov, O.V. Lebedev, L.I. Khmel'nitskii and Iu. P. Egorov	2342	2305
Errata	2345	

JOURNAL OF GENERAL CHEMISTRY OF THE USSR

Volume 28, Number 9 September 1958

CONTENTS

	PAGE	RUSS. PAGE
Synthesis of Hydrocarbons. LXVI. C$_{11}$-C$_{16}$ Hydrocarbons with Two Adjacent Quaternary Carbon Atoms. R. Ia. Levina, P. A. Kaikaris, A. V. Simolin, and E. G. Treshchova . . .	2347	2309
Reaction of Tert-Butylbenzene β-(Magnesium Chloride) with Carbonyl Compounds. A. D. Petrov, G. I. Nikishin, V. N. Gramenitskaia, and V. D. Vorob'ev	2353	2315
Investigations of Conjugated Systems. XCII. Sequence of Addition of Iodine to Vinylacetylenic Hydrocarbons. A. A. Petrov. Iu. I. Porfir'eva, T. V. Iakovleva, and K. S. Mingaleva	2357	2320
Investigations on Conjugated Systems. XCIII. The Sequence of Addition of Alkyl Hypobromites to Vinylalkylacetylenes. A. A. Petrov, Iu. I. Porfir'eva, and G. I. Semenov . . .	2362	2325
The Vapor-Phase Catalytic Hydration of Acetylene and Its Homologs. III. Study of the Process of Catalytic Hydration of Acetylene Over Some Solid Catalysts. Iu. A. Gorin and I. K. Gorn.	2366	2328
Investigations on Polymethylene Rings. XXXII. Transformations of Cyclohexene in Conjugated Halogenations and Dehalogenations. N. A. Domnin and V. A. Cherkasova	2371	2334
Investigation of the Exchange of Oxy Radicals for the Hydrocarbon Radicals of Organomagnesium Compounds. IV. Interaction of Grignard Reagents with Organic Acylals. M. F. Shostakovskii and M. R. Kulibekov	2376	2339
Synthesis and Transformations of α-Substituted Vinyl Ethers. VII. Synthesis and Transformations of α-Chloroisopropyl Aryl Ethers. M. F. Shostakovskii, E. P. Gracheva, and N. K. Kul'bovskaia	2379	2341
Synthesis and Transformations of α-Substituted Vinyl Ethers. VIII. Some Properties of α-Methylvinyl Aryl and α-Methylvinylcyclohexyl Ethers. M. F. Shostakovskii, E. P. Gracheva, and N. K. Kul'bovskaia	2382	2344
Synthesis and Study of N-Oxides of Heterocyclic Compounds. I. N-Oxide Derivatives of Morphine, Tetrahydroisoquinoline and Quinoline. A. M. Khaletskii, V. G. Pesin, and Chou Ts'in	2386	2348
Chemistry of Pyrazolidine. I. Synthesis and Study of Some Mono- and Disubstituted Derivatives of 1,2-Diphenyl-3,5-dioxopyrazolidine. A. M. Khaletskii, V. G. Pesin, and Têng Jun-hsiang	2393	2355
Reaction of Ammonia and Amines with Oxides of Acetylenic and Vinylacetylenic Series. New Method for the Preparation of Pyrrole Homologs. F. Ia. Perveev and E. M. Kuznetsova	2397	2360

CONTENTS (continued)

	PAGE	RUSS. PAGE
Tetraacyloxysilanes in Organic Synthesis. XVII. Acylation of Benzene with the Silicoanhydrides of Acetic, Mono-, Di- and Trichloroacetic and β-Bromopropionic Acids. Iu. K. Iur'ev, Z. V. Beliakova, and V. P. Volkov	2408	2372
Ethylene Sulfide in the Synthesis of Heterocyclic Compounds with Two Hetero Atoms. VIII. Synthesis of 2-(2-Furyl)-, 2-(2-Thienyl)-, and 2-(2-Selenienyl)-3-arylthiazolidines. Iu. K. Iur'ev and S. V. Diatlovitskaia	2413	2377
Condensation of γ,γ,γ-Trichlorocrotononitrile with Benzene in the Presence of Aluminum Chloride. A. D. Grebeniuk and I. P. Tsukervanik	2417	2380
Catalytic Amination of Organic Compounds. VII. Catalytic Transformations in the Butylamine Series. N. S. Kozlov and N. I. Panova	2421	2384
Properties of Binary Mixtures of Organic Compounds as a Function of Association and Concentration. A. E. Lutskii, E. M. Obukhova, and I. A. Sidorov	2423	2386
Effect of Dilution on the Activity of Copper Catalyst in the Dehydrogenation of Butyl Alcohol. B. N. Dolgov, V. V. Mazurek, and V. A. Krol'	2433	2395
Some N-ω-Phenylalkyl-β-chloropropionamides. N. K. Kochetkov and N. V. Dubykina	2437	2399
Reaction of p-Halophenylhydrazines with Arsenic Acid. O. A. Zeide, S. M. Sherlin, and A. B. Bruker	2442	2404
New Method for the Preparation of Organoarsenic Compounds by the Oxidation of a Mixture of Phenylhydrazine and Arsenic Trichloride with Atmospheric Oxygen in the Presence of Cupric Chloride. A. B. Bruker and N. M. Nikiforova	2445	2407
Preparation of Esters of Fluoroantimonious and Fluorotitanic Acids by Treatment of the Complete Esters of These Acids with Antimony Trifluoride. A. B. Bruker, R. I. Frenkel', and L. Z. Soborovskii	2450	2413
Investigation of a Series of Organic Sulfur Compounds. IV. Synthesis of β-Chloroethanesulfonyl Chloride. B. M. Gladshtein, I. P. Kuliulin, and L. Z. Soborovskii	2454	2417
Investigation in the Field of Alkanesulfonic Acids. XVIII. Chlorination of Alkanesulfonic Acid Toluidides. A. G. Kostsova and N. T. Borisova	2457	2420
Alkylation Over an Aluminosilicate Catalyst Activated by Gaseous Hydrogen Chloride. I. Alkylation of Benzene by Alkyl Chlorides. I. F. Radzevenchuk	2461	2423
Dependence of the Yield and the Quality of Benzenesulfonyl Chloride on the Excess of Chlorosulfonic Acid and Addition of Sodium Salts. L. I. Levina, S. N. Patrakova, and D. A. Patrushev	2464	2427
Acetals of β,β-Dihalo Substituted Propionaldehydes. T. V. Protopopova and A. P. Skoldinov	2466	2428
Heterocyclic Compounds. LXII. Stereochemistry of 1-Acyl-2,5-Dimethyl-4-Piperidones. I. N. Nazarov, N. S. Prostakov, and N. N. Mikheeva	2469	2431
Condensation of Acetals with 1-Ethoxydienes. A New Method of Synthesis of Polyene Aldehydes of Isoprene Type. I. N. Nazarov and Zh. A. Krasnaia	2477	2440
Synthesis of Dienic Acids from α-Pyrones. L. I. Kudriaskhov and N. K. Kochetkov	2484	2448
Diphensuccindane and 2,6-Dihydroxydiphensuccindane. S. F. Torf and N. V. Khromov-Borisov	2488	2452

CONTENTS (continued)

	PAGE	RUSS. PAGE
Studies in the Series of Isoquinoline Compounds. XIV. Esters of Isomeric 4',5'-Dimethoxy-6-ethyl-3,4,5,6,7,8-hexahydrobenzo-(1,2:1',2')-quinolizyl-7-acetic Acids. R. P. Evstigneeva	2494	2458
Studies in the Series of Isoquinoline Compounds. XV. Synthesis of Isomeric o-Methylpsychotrines. R. P. Evstigneeva, R. G. Glushkov, and N. A. Preobrazhenskii	2499	2463
From the Field of Organic Insectofungicides. XXXIV. New Method of Synthesis of Trialkyl Phosphites. N. N. Mel'nikov, Ia. A. Mandel'baum, and Z. M. Bakanova	2507	2473
Catalytic Synthesis of Ketones. V. Synthesis of Methyl Phenyl, Ethyl Phenyl, Methyl n-Propyl, and Di-n-propyl Ketones. I. P. Iakovlev and D. P. Popa	2510	2475
Reaction of Phosphorus Pentachloride with Amides of Phosphoric Acid. A. V. Kirsanov and I. N. Zhmurova	2514	2478
Direct Azo Dyes – Derivatives of 1,8-Naphtholylene-1',2'-benzimidazole. B. M. Krasovitskii, R. M. Matskevich, N. A. Radochina, and K. P. Riazanova	2520	2485
Replacement of Halogen in Azo Compounds. III. Preparation of Derivatives of o-Arylalkoxyanilines. B. I. Stepanov and M. A. Andreeva.	2525	2490
Anomalous Reaction of Phosphites with α-Halo Ketones. VIII. Reactions of Mixed Phosphites with Chloro- and Dichloroacetones. A. N. Pudovik and E. G. Chebotareva.	2527	2492
Addition of Ammonia and Amines to Isoprene Oxide. A. N. Pudovik and I. M. Aladzheva. . .	2532	2497
The Problem of Synthesis of Di-β,β'-chloroethyl Ester of Vinylphosphonic Acid. E. L. Gefter.	2536	2500
A New Method of Introduction of Trihalomethyl Group Into Organic Compounds. N. N. Iarovenko and A. S. Vasil'eva	2539	2502
Preparation of Esters of N-Trifluoromethylthiolcarbamic Acid. N. N. Iarovenko and S. P. Motornyi	2541	2504
Properties of Heteroorganic Compounds in the Light of D. I. Mendeleev's Periodic System. I. Boiling Points of Compounds of Fluorine and Other Halogens. N. N. Iarovenko	2543	2506
Studies in the Field of Isoquinolinecarboxylic Acids. I. Preparation of 7,8-Dimethoxyisocarbostyryl-3-carboxylic Acid, Its Esters and 7,8-Dimethoxyisocarbostyryl. L. I. Linevich.	2547	2510
Studies in the Field of Isoquinolinecarboxylic Acids. II. Preparation of 1-Chloro Substituted Carboxylic Acid of the Isoquinoline Series, Its Chloride and Esters and Some Data on Mobility of Chlorine in 1-Position of the Isoquinoline Nucleus. L. I. Linevich	2551	2514
Synthesis of Amino Acids of Aliphatic Series from Thiophene Derivatives. III. Synthesis of ω-Amino Acids. B. P. Fabrichnyi, I. F. Shalavina, and Ia. L. Gol'dfarb	2556	2520
Synthesis of Some Adrenaline Derivatives. I. Synthesis of D,L-Adrenaline and Its Analogs. A. L. Remizov	2566	2530
Synthesis of Thiacarbocyanines with Unsaturated Radicals as Substituents. M. A. Al'perovich, I. K. Ushenko, and L. N. Tiurina	2573	2538
Liquid Phase Oxidation of Alkylaromatic Hydrocarbons with Atmospheric Oxygen. Oxidation of p-Cymene and p-Sec-Butyltoluene. V. V. Fedorova and P. G. Sergeev	2581	2547
Liquid Phase Oxidation of Alkaromatic Hydrocarbons with Atmospheric Oxygen. Oxidation of p-Di-Sec-Butylbenzene. V. V. Fedorova and P. G. Sergeev	2586	2552

CONTENTS (continued)

	PAGE	RUSS. PAGE
A New Method for the Preparation of Quinaldine Bases and N-Arylquinaldinium Salts by the Condensation of Arylamines with Aldehydes. XX. V. I. Minkin and B. I. Ardashev. . . .	2590	2556
Reaction of Diazo Compounds with Sulfamic Acid and Its Derivatives. XI. Causes of the Coloration of Some Diazonium and Heterocyclic Ammonium Salts. D. Z. Zavel'skii and L. A. Lishnevskaia	2594	2560
Reaction of Diazo Compounds with Sulfamic Acid and Its Derivatives. XII. Diaryltriazene-N-sulfonic Acids and Their Diazonium Salts. D. Z. Zavel'skii and L. A. Lishnevskaia .	2602	2568
Investigations in the Field of Organocyclosiloxanes. III. The Use of the Method of Thermo-oxidative Destruction for the Investigation of the Hydrolysis Products of Alkyltrichlorosilanes. N. N. Sokolov	2611	2578
The Synthesis of o-Carboxy- and o-Carboxydimethoxybenzalbarbituric Acids. E. I. Chukhina	2616	2582
The Synthesis of Substances with a Hypotensive Action, Derivatives of Quaternary Ammonium Bases. IV. Quaternary Salts of β-Phenylisopropyldimethylamine. I. B. Simon	2619	2586
The Reactivity of α,β-Unsaturated Ketones and β-Ketone Halides in the Kizhner Reaction. A. P. Meshcheriakov, L. V. Petrova, and Iu. P. Egorov	2621	2588
The Investigation of Triterpenes. II. The Structure of Zeorin. A. A. Riabinin and L. G. Matiukhina	2628	2595
The Condensation Products of L-Ephedrine and D-Pseudoephedrine with Acetone. L. G. Matsova and A. S. Labenskii	2631	2598
Hormones of the Thyroid Gland and Their Analogs. IV. The Synthesis of Desamino Analogs of Betazine (β-Diiodotyrosine). N. N. Suvorov, L. M. Morozovskaia, and A. A. Dudinskaia	2634	2601
The Spectrophotometric Investigation of the Reaction of Chlorophyll with Ferric Chloride. S. S. Butsko and B. Ia. Dain	2636	2605
Further Discussion. The Problem of the General Definition of Chemistry. Iu. A. Zhdanov . .	2643	2611
Academy of Sciences USSR Press "Akademkniga" Bureau	2645	back cover

JOURNAL OF GENERAL CHEMISTRY OF THE USSR

Volume 28, Number 10 October 1958

CONTENTS

	PAGE	RUSS. PAGE
The Properties of Salt-Form Compounds of Variable Composition and Views on Their Chemical Structure. S.M. Ariia and M.P. Morozova	2647	2617
Study of Double Sulfates of Americium by Absorption Spectra of Crystals. G.N. Iakovlev, D.S. Gorbenko-Germanov, R.A. Zenkova, V.M. Razbitnoi and K.S. Kazanskii	2653	2624
Hydrogen Exchange in Phenol, Its Ethers and Aromatic Amines with Liquid DBr. A.I. Shatenshtein, A.V. Vedeneev and P.P. Alikhanov	2666	2638
Hydrogen Exchange of Phenol and Its Ethers with Solutions of Potassamide in Liquid Deuteroammonia. A.I. Shatenshtein and A.V. Vedeneev	2672	2644
Isotope Exchange of 2-Mercaptobenzthiazole Sulfur and Elementary Sulfur in the Presence of Amines. G.A. Blokh and V.S. Zdanovich	2680	2652
Dehydrogenation Kinetics of Cyclohexane and Its Homologs on a Chromium Catalyst at Atmospheric Pressure. G.N. Maslianskii and N.R. Bursian	2684	2656
A Study of the Dehydrogenation of Cyclohexane on a Chromium Catalyst Under a Pressure of Hydrogen. G.N. Maslianskii and N.R. Bursian	2690	2663
Alkylation of Isopropylbenzene by Pseudobutylene in the Presence of $BF_3 \cdot H_3PO_4$. S.V. Zavgorodnii and L.S. Shvetsova	2695	2668
Derivatives of Benz-(c,d)-indoline. I. Thionaphthostyryl and N-Methylthionaphthostyryl. N.S. Dokunikhin and L.A. Gaeva	2698	2670
The Preparation of o-Nitrosophenol from Salicylic Acid. A.A. Nemodruk	2701	2672
The Replacement of Halogen in Azo Compounds. IV. The Replacement of Chlorine in 5-Methyl-2-chlorobenzeneazo-2'-naphthol by Alkoxy and Aroxy Groups and the Preparation of Ethers of 3-Amino-4-hydroxytoluene. B.I. Stepanov	2705	2676
Investigation of the Products from the Reaction of Epichlorohydrin and Aromatic Amines. III. The Action of Hydrochloric Acid and Thionyl Chloride on 3-Hydroxy-1,2,3,4-tetrahydro-7,8-benzoquinoline and on 3-Hydroxy-1,2,3,4-tetrahydro-5,6-benzoquinoline. N.N. Vorozhtsov, Jr. and S.I. Kutkevichus	2710	2682
The Process of Polyamide Resin Formation. VII. The Composition and Structure of Salts Formed by Dicarboxylic Acids and Diamines or Hydrazine. A.S. Shpital'nyi and Ia.A. Kharit	2715	2687
Investigation of Heterocyclic N-Oxides. VI. Polarographic Reduction of Some N-Oxides of Phenazines and Acridines. O.N. Nechaeva and Z.V. Pushkareva	2721	2693
Investigation of Heterocyclic N-Oxides. VII. Dipole Moments and Chemical Features of Some Derivatives of Phenazine and Acridine N-Oxides. Z.V. Pushkareva and O.N. Nechaeva	2729	2702

CONTENTS (continued)

	PAGE	RUSS. PAGE
Investigation of Structural Features and Chemical Conversions of Carbazole and Some of Its Derivatives. II. Some Features of 3-Aminocarbazole and Its Derivatives. S.I. Omel'chenko and Z. V. Pushkareva	2733	2706
Catalytic Dehydrocondensation of Trialkylsilanes with Alcohols in the Presence of Metal Chlorides. B.N. Dolgov, N.P. Kharitonov, N.E. Glushkova and Iu.I. Khudobin	2737	2710
Catalytic Dehydrocondensation of Trialkylsilanes with Glycols. B.N. Dolgov, N.P. Kharitonov and T.V. Tsukshverdt	2741	2714
The Mechanism of Acid Oxidation by Molecular Oxygen in an n-Heptane Medium. I.V. Verezin, B.I. Makalets and L.G. Chuchukina	2746	2718
Thermocatalytic Conversions of α-Methylnaphthalene. B.G. Gavrilov and M.I. Buzanov	2750	2723
Some Considerations on the Mechanism of the Formation of Mercuryaromatic Compounds by the Oxidation of Arylhydrazines with Mercuric Salts. A.B. Bruker and B.B. Levin	2752	2725
Halogenation of Aromatic Silanes. VI. Preparation and Properties of Chloro Derivatives of p-(Trichloromethyl)-phenyltrichlorosilane. G.V. Motsarev and A.Ia. Iakubovich	2754	2727
Reaction of β-Chlorovinyl Ketones with β-Dicarbonyl Compounds. VII. Acid Cleavage of α-Alkyl-α-(3-ketoalkenyl)-acetoacetic Esters. N.K. Kochetkov and B.P. Gottykh	2759	2732
Investigation in the Isoxazole Series. VII. Chloromethylation of Isoxazoles. N.K. Kochetkov, E.D. Khomutova and M.V. Bazilevskii	2762	2736
Heterocyclic Compounds. 63. Synthetic Analgesics. XXVI. Stereoisomerism of 2,5-Dimethyl-4-piperidols and 1-Acyl-2,5-dimethyl-4-phenyl-4-piperidols. I.N. Nazarov, N.S. Prostakov and N.N. Mikheeva	2771	2746
Acetylene Derivatives. CXCIV. Hydration of Divinylacetylene and Vinylisopropenylacetylene in Alcohol Solutions. I.N. Nazarov, S.A. Vartanian and S.G. Matsoian	2781	2757
Tetraacyloxysilanes in Organic Synthesis. XVIII. Structure of the Silicoanhydrides of Dibasic Saturated Organic Acids. Iu.K. Iur'ev, Z.V. Beliakova and G.B. Eliakov	2789	2766
Tetraacyloxysilanes in Organic Synthesis. XIX. Synthesis of 3- and 4-Nitrocinnamic Acids, and Their Homologs [α-Alkyl-β-(nitrophenyl)acrylic Acids]. Iu.K. Iur'ev, A.N. Vysokosov and S.N. Godovikova]	2793	2770
Reactions of Hydrazine Derivatives. XIX. Condensation of 4-Amino-[1,2,4]-triazole with Esters. A.N. Kost and F. Gents	2796	2773
Reaction of Arylsulfonamides with Propylene Oxide. A.E. Kretov and E.A. Abrazhanova	2802	2779
Study of the Isomerization and Dimerization of Dimethylvinylcarbinol as a Function of the pH of the Reagent. IV. The Structure of a New Isomer of Geraniol. A.I. Lebedeva and L.V. Kukhareva	2806	2782
Synthesis of Hydrazides and Hydrazones of Some Heterocyclic and Aromatic Acids. E.S. Nikitskaia, E.E. Mikhlina, L.N. Iakhontov and V.Ia. Furshtatova	2810	2786
Addition of Neutral Esters of Phosphorous and Phosphonous Acids to Conjugated Systems. VI. Joint Reaction of Alkyl Halides and α,β-Unsaturated Acids with Trialkyl Phosphites. V.A. Kukhtin and K.M. Orekhova	2814	2790
1-Aminomethyl-4-phthalazone. M.A. Matskanova and G.Ia. Vanag	2822	2798

CONTENTS (continued)

	PAGE	RUSS. PAGE
Compounds with Two Geminate Indandione Groups in the Molecule. II. Condensation of 5,6-Dinitroacenaphthenequinone with 1,3-Indandione. L.S. Geita and G.Ia. Vanag.	2825	2801
β,β-Dihalopropionaldehydes. T.V. Protopopova and A.P. Skoldinov.	2829	2805
N-Arylsulfonamide Derivatives of Diethanolamine. A.E. Kretov and G.V. Tikhonova.	2832	2808
Ethers of Glycols and Their Derivatives. XXXV. Synthesis of β,γ-Dibromo Derivatives of Ethers of Methylene Glycol. Shamkhal Mamedov and D. Khydyrov.	2836	2812
Chemistry of Pyrazolidine. II. Halogenation and Thiocyanation of 1,2-Diphenyl-3,5-dioxopyrazolidine and Its Derivatives. V.G. Pesin, A.M. Khaletskii and Teng Jun-hsiang. . .	2841	2816
Synthesis and Investigation of N-Oxides of Heterocyclic Compounds. II. N-Oxides of Acridine Derivatives. A.M. Khaletskii, V.G. Pesin and Chou Ch'ing	2845	2821
Synthesis of Hydrocarbons. LXVII. C_{12} Hydrocarbons with One and Two Quaternary Carbon Atoms. R.Ia. Levina, P.A. Kaikaris and P.A. Gembitskii	2849	2825
Interaction of γ-Chloropropylsilane Chlorides with Aromatic Compounds by Friedel–Crafts Reaction. E. A. Chernyshev, M. E. Dolgaia and Iu. P. Egorov	2853	2829
Synthesis of β-Chloroethyl Phenyl Acetal. M.F. Shostakovskii, M.R. Kulibekov and A.K. Gorban'.	2862	2838
Synthesis of γ,γ'-Diphenyldipropyl Acetal. M.F. Shostakovskii, M.R. Kulibekov and A.K. Gorban'.	2864	2839
Investigations in the Field of the Synthesis and Conversions of Oxygen-Containing Organosilicon Compounds. On the Interaction of Vinylalkylchlorosilanes with Vinyl Butyl Ether and Vinyl Lactams. M.F. Shostakovskii, D.A. Kochkin, V.A. Neterman and F.P. Sidel'kovskaia	2866	2840
Synthesis of Alkenyl-α-CN-isopropoxysilanes. V.M. Vdovin and A.D. Petrov.	2868	2842
Organomagnesium Synthesis with Carbon Suboxide. I. L.B. Dashkevich and E.I. Boksiner. . . .	2872	2845
The Effect of Low Molecular Weight Materials on the Photochemical Degradation of Polyethylene Terephthalate. V.V. Korshak, K.K. Mozgova and A.P. Zasechkina.	2874	2847
The Interaction of Phenylphosphorus Tetrachloride with Diazomethane. L.M. Iagupol'skii and P.A. Iufa	2880	2853
Synthesis of 6-Bromo-8-mercaptoquinoline (6-Bromothiooxine) and Some of Its Properties. Iu.A. Bankovskii and E.F. Lobanova	2884	2857
The Number of Optical Stereoisomers and Their Distribution with Respect to the Different Types of Configuration in Compounds with Continuous Series of Asymmetric Centers in an Unbranched Chain. L.A. Mai.	2887	2860
Reactions of Pyridinium Salts. II. Interaction of Chloro-2,4-dinitrophenylates of Substituted Pyridine Bases with Aniline. A.F. Vompe and N.F. Turitsyna	2891	2864
On Some Properties of Enol Acetates. III. Preparation of Furan and Pyran Derivatives from Bromo-Substituted Enol Acetates. I.V. Machinskaia and V.A. Barkhash.	2899	2873
On the Synthesis and Structure of the o-Sulfobenzoyl Dichlorides. D.Sh. Rozina, L.T. Nesterenko and Iu.I. Vainshtein.	2904	2878

CONTENTS (continued)

PAGE RUSS. PAGE

The Preparation of Δ^{23}-3-Keto-24,24-diphenylcholene. V.I. Maksimov, F.A. Lur'i and G.P. Krupina. 2910 2883

The Preparation of Pregnane-3,20-dione from Δ^{23}-3-Keto-24,24-diphenylcholene-3-ethylene Ketal. V.I. Maksimov, F.A. Lur'i and G.P. Krupina 2913 2886

A New Alkaloid from the Central Asiatic Larkspur. A.V. Bocharnikova and E.I. Andreeva. . . 2918 2892

Preparation of Hydratropic Alcohol. A.M. Sladkov and L.K. Luneva. 2921 2894

Electrosynthesis of Nicotinic Acid. V.G. Khomiakov, S.S. Kruglikov and V.M. Berezovskii . . 2925 2898

Discussion Series. Conjugation in, and the Dual Reactivity of, Butadiene. M.I. Batuev. 2930 2903

JOURNAL OF GENERAL CHEMISTRY OF THE USSR

Volume 28, Number 11 November 1958

CONTENTS

	PAGE	RUSS. PAGE
Thermographic Investigation of the Regeneration of Chromium Catalysts. T. V. Rode and A. A. Balandin	2937	2909
Physicochemical Analysis of the System Formic Acid – Dimethylformamide. Density, Viscosity, and Electrical Conductivity in the System Formic Acid – Dimethylformamide. M. D. Korol'kova and B. K. Kricheviov	2943	2915
The Ternary Mutual System of the Propionates and Nitrates of Sodium and Potassium O. I. Dmitrevskaia and N. M. Sokolov	2949	2920
Polytherm of the Ternary System Urea – Citric Acid – Water. V. P. Blidin and T. G. Golovanova	2955	2926
Polarographic Determination of Nitriles. M. I. Bobrova and A. N. Matveeva-Kudasheva . .	2958	2929
Cyclic Esters of Antimonous Acid. O. D. Dubrovina-Samoilova	2962	2933
New Regularities in the Physicochemical Properties of Hydrocarbons. III. Heats of Crystallization of n-Alkanes. B. M. Tatevskii	2965	2935
The Proton Mobility of Hydrogen Atoms in Aromatic Hydrocarbons with Aliphatic Substituents. A. I. Shatenshtein and E. A. Izrailevich	2969	2939
Benz[c,d]indoline Derivatives. II. 6-Benzoylbenz[c,d]indoline-2-one, 1-Methyl-6-Benzoylbenz[c,d]indoline-2-one and the Products of Their Cyclization. N. S. Dokunikhin and L. A. Gaeva	2974	2944
Chemistry of Xanthates and Viscose. VIII. Investigation of Polythio Compounds and of the Composition of Viscose, Using Labelled Atoms. S. N. Danilov, N. F. Gintse and K. V. Levitskaia	2978	2948
Reactions of Sulfur and Inorganic Sulfides with Dialkyltrichlorophosphine – Aluminum Chloride Adducts. S. Z. Ivin and K. V. Karavanov	2988	2958
Reactions of Sulfur and Inorganic Sulfides with Aluminum Chloride Adducts of Alkyltetrachlorophosphine. I. P. Komkov, S. Z. Ivin and K. V. Karavanov	2990	2960
New Methods of Preparing Alkyldichlorophosphines and Dialkylchlorophosphines. I. P. Komkov, K. V. Karavanov and S. Z. Ivin	2992	2963
Halogen Displacement in Azo Compounds. V. Reaction of the Copper Complex of 2-Chlorobenzeneazo-2'-naphthol with Alkoxides. M. A. Andreeva and B. I. Stepanov	2995	2966
Halogen Displacement in Azo Compounds. VI. Substitution of Chlorine by a Methoxy Group in 2-Hydroxy-8'-chloro-(1,1')-azonaphthalene and in Its Copper Complex. B. I. Stepanov and V. A. Savel'ev	2997	2968

CONTENTS (continued)

	PAGE	RUSS. PAGE
Some Ethylenimino-1,3,5-triazines. G. I. Braz, V. K. Antonov and K. N. Kurdiumova . .	3001	2972
Some Derivatives of Phenoxazone. R. S. Chlenova, Ts. M. Gel'fer and S. F. Petrov	3006	2977
Dehydrogenation of α-Tetralone with Selenium and Synthesis of 1-Naphthol-1-C^{14}. N. N. Vorozhtsov, Jr., and V. A. Koptiug	3010	2981
Reactions Involving Organic Solids. XI. The Influence of Temperature on the Conversion of N-Arylamic Acids into Imides. M. Kh. Gluzman	3016	2987
Cycloalkylation of Phenols and Their Ethers. I. Condensation of Phenol with Cyclohexanol. A. R. Abdurasuleva	3022	2993
Mercaptoamines. I. β-Mercaptoethylamine and its N-Substituted Derivatives. F. Iu. Rachinskii, N. M. Slavachevskaia and D. V. Ioffe	3027	2998
Chlorination of Olefin Chlorohydrins. I. F. Spasskaia, V. S. Etlis and G. A. Razuvaev . . .	3033	3004
Reaction of Mercuric Pivalate with Peroxides and with Light. Iu. A. Ol'dekop and T. V. Vasilevskaia	3037	3008
Synthesis of Acetylcholine Labelled with Radioactive Carbon C^{14} in the Ester Group. L. B. Dashkevich and V. S. Karpinskii	3040	3011
Cycloserine and Related Compounds. III. Synthesis of Cycloserine. N. K. Kochetkov, R. M. Khomutov, M. Ia. Karpeiskii and E. I. Budovskii	3042	3013
A New Reaction of α-Pyrones. Synthesis of Vinylogs of β-Oxo Acid Esters. N. K. Kochetkov and L. I. Kudriashov	3049	3020
Synthesis of Aliphatic β-Chlorovinyl Ketones from Hydroxymethylene Ketones. N. K. Kochetkov, Ivan Ambrush, T. I. Ambrush and E. S. Severin	3053	3024
Studies in the Field of Chemistry of Pyrazolidine. III. Study of the Reactivity of 1,2-Diphenyl-3,5-Dioxopyrazolidine (Nitration, Sulfonation etc.). A. M. Khaletskii, V. G. Pesin and Têng Jun-Hsiang	3057	3027
Studies in the Field of Chemistry of Pyrazolidine. IV. Synthesis and Study of Sulfides and Disulfides of 1,2-Diphenyl- and n-Butyl-1,2-diphenyl-3,5-dioxopyrazolidines. V. G. Pesin, A. M. Khaletskii and Têng Jun-Hsiang	3060	3030
Chemistry of Selenophene. XIII. Cyanoethylation of Ketones of the Selenophene Series. Iu. K. Iur'ev, N. K. Sadovaia and V. V. Titov	3066	3036
Chemistry of Selenophene. XIV. Reactions of Selenophene-2-aldehyde. Iu. K. Iur'ev and N. N. Mezentsova	3071	3041
Catalytic Hydrogenation of Vinylethylene Oxides. I. Hydrogenation of Butadiene Oxide. M. A. Aizikovich, I. A. Maretina and A. A. Petrov	3076	3046
Catalytic Hydrogenation of Vinylethylene Oxides. II. Hydrogenation of Chloroprene Oxide. M. A. Aizikovich and A. A. Petrov	3082	3051
On Reaction of Dialkyl Hydrogen Phosphites with Aldehydes and Ketones. XVIII. Phenyl Esters of α-Hydroxyalkylphosphonic Acids. V. S. Abramov and N. A. Semenova . . .	3087	3056
On the Reaction of Aryl(alkyl)phospinic Acids with Aldehydes and Ketones. XIX. Esters of α-Hydroxyalkylphenylphosphinic Acids. V. S. Abramov and M. I. Kashirskii	3090	3059

CONTENTS (continued)

	PAGE	RUSS. PAGE
Diene Condensations of Gem-Substituted Butadienes. I. I. N. Nazarov and M. V. Mavrov	3092	3061
Reactions of Hydrazine Derivatives. XX. Dehydrogenation of Pyrazolines. I. I. Grandberg and A. N. Kost	3102	3071
Addition of Organomagnesium Compounds to Isopropylidenemalonic Ester. V. P. Gol'mov and Z. P. Malevannaia	3106	3075
Triaminopyridothiazole and the Products of Its Condensation with Dicarbonyl Compounds. S. G. Fridman	3109	3078
2-Diphenylacetyl-1,3-indanedione. Ia. K. Ozol, V. N. Zelmen and G. Ia. Vanags	3114	3083
Synthesis of 2-(α-pyridyl)-3-(β-hydroxyethyl)-indole. Chên Chang-Pai, R. P. Evstigneeva and N. A. Preobrazhenskii	3116	3085
Comparative Study of Chemical Structure of SKB Rubber and SKBM Rubber by the Method of Ozonolysis. A. I. Iakubchik, A. I. Spasskova, A. G. Zak and I. D. Shostatskaia	3121	3090
Catalytic Ionic Telomerization. II. The Composition of the Fraction of Terpene Chlorides in the Product of Telomerization of Isoprene with Its Hydrochlorides. Linalyl Chloride. K. V. Leets	3127	3096
The Condensation of 1-Heptyne with Chloral. N. E. Kologrivova and V. N. Belov	3136	3105
Reduction of Derivatives of Harmine with Sodium Borohydride to Derivatives of Py-Tetrahydroharmine. L. N. Iakhontov and M. V. Rubtsov	3139	3108
Synthesis of 1-Phenyl-3-pyrazolidone (Phenidone) from Esters of β-Chloropropionic Acid. V. N. Mikhailova and V. V. Pigulevskii	3142	3112
The Synthesis of 4-Aminopiperidine. L. N. Iakhontov, S. V. Iatsenko and M. V. Rubtsov	3146	3115
The Glycosidic Alkaloid of the Plant Solanum Megaparcum Koidz. (Large-Fruited Nightshade). A. S. Labenskii, I. I. Gerasimenko and L. M. Utkin	3150	3120
Organic Insectofungicides. XXXV. Reaction of 1,1-Difluorotetrachlorocyclopentadiene with some Unsaturated Compounds. S. D. Volodkovich, N. N. Mel'nikov, A. F. Plate and M. A. Prianishnikova	3153	3123
Investigation of Aconite Alkaloids. XIII. The Alkaloids of Aconitum Rotundifolium Kar. and Kir. and Aconitum Nemorum M. Pop. [1]. T. F. Platonova, A. D. Kuzovkov and P. S. Massagetov	3157	3126
Alkaloids of the Chenopodiaceae (Gooseroot). Anabasis Jazartica and Arthrophytum Leptocladum. T. F. Platonova, A. D. Kuzovkov and P. S. Massagetov	3159	3128
Alkaloids of Plants of the Family of the Asclepiadaceae (Milkweed). I. Antitoxicum Funebre (Boiss. Et Ky.) Pobed. T. F. Platonova, A. D. Kuzovkov and P. S. Massagetov	3162	3131
Spectrophotometry of Biuret Complexes as a Method of Investigation of Polypeptides and Proteins. XIX. Some Double Decomposition Reactions of Copper-Biuret Complexes. M. I. Plekhan	3164	3133
Study of the Structure of Some Fructosans of Plants of the Family Liliaceae. S. M. Strepkov	3173	3143
Discussion Forum. The Problem of Conjugation in Benzene. M. I. Batuev	3177	3147
New Books	3186	Back Cover

JOURNAL OF GENERAL CHEMISTRY OF THE USSR

Volume 28, Number 12 December 1958

CONTENTS

	PAGE	RUSS. PAGE
Letter to Stepan Nikolaevich Danilov	3189	
Stepan Nikolaevich Danilov (For his seventieth birthday and the forty-fifth anniversary of his scientific and teaching activity). N. A. Domnin	3190	3157
The Works of S. N. Danilov in the Field of Isomeric Conversions and Molecular Rearrangements of Carbonyl and Hydroxycarbonyl Compounds and Carbohydrates and Their Theoretical Importance. T. I. Temnikova, A. N. Anikeeva and N. S. Tikhomirova-Sidorova	3194	3162
The Works of S. N. Danilov in the Field of Cellulose and its Ethers and Esters. E. A. Plisko, M. G. Okun', N. M. Grad and N. F. Gintse	3203	3174
Anhydro, Desoxy and Unsaturated Derivatives of Polysaccharides. I. Desoxycellulose from Cyanoethoxylcellulose. S. N. Danilov and A. A. Lopatenok	3213	3184
Anhydro, Desoxy and Unsaturated Derivatives of Polysaccharides. II. The Synthesis of Anhydrocellulose from p-Toluenesulfonic Esters. S. N. Danilov and A. A. Lopatenok	3218	3189
The Chemistry of Xanthates and Viscose. IX. The Detection of Polysulfide Compounds in Viscose and their Role. S. N. Danilov, N. F. Gintse and M. G. Okun'	3221	3192
The Formation of Peroxides in the Oxidation of Cellulose Ethers and Esters. O. P. Koz'mina, V. I. Kurliankina, E. N. Matveeva and M. K. Aleksandrovich	3230	3202
Allyl and Methallyl Esters of Acetals and Ketals of Xylitol and Xylitan. A. N. Anikeeva and G. M. Zarubinskii	3233	3206
Amino Derivatives of 1,4-Anhydroxylitol. N. S. Tikhomirova-Sidorova and G. E. Ustiuzhanin	3238	3210
A Search for New Methods of Synthesizing Cellulose Ethers. E. A. Plisko	3242	3214
Comparative Distribution of Carbon Disulfide in the Main and Side Reactions in the Preparation of Viscose at Low Temperature and Under Normal Conditions. E. A. Abramova	3245	3217
Investigations in the Field of Conjugated Systems. XCV. Reactions of Piperylene with its Hydrochloride and with the 1,4-Hydrochloride of Isoprene. A. A. Petrov, N. A. Razumova and M. L. Genusov	3248	3220
Chemical Conversions of α-Halo Ketones. VI. The Action of Sodium Phenolate and Cresolate on α-Bromocyclohexanone. T. I. Temnikova and N. A. Oshueva	3252	3224
An Investigation of the Conversions of Secondary-Tertiary α-Glycols of the Acetylene Series Under the Action of Mercury Salts. III. 2-Methyl-1,4-diphenylbutyne-3-diol-1,2. A. Fabritsy and E. D. Venus-Danilova	3255	3227

CONTENTS (continued)

	PAGE	RUSS. PAGE
The Mechanism of Dehydration of γ-Glycols. VI. Study of the Dehydration of 3-Methylhexyne-1-Diol-3,6. T. A. Favorskaia and O. V. Sergievskaia	3260	3232
Homologs of Monovinylacetylene. VIII. Spectral Characteristics of an Enyne Hydrocarbon – 3',3'-Metho-3-ethylbuten-3-yne-1 – and its Derivatives. Iu. P. Artsybasheva and I. A. Favorskaia	3266	3238
The Cyanoethylation of Acetylene γ-Glycols. A. I. Zakharova and A. M. Efros	3270	3243
The Reaction of Nitrosyl Chloride with Unsaturated Hydrocarbons. IV. The Reaction with Butene-1. K. A. Ogloblin	3272	3245
Investigation in the Field of Compounds Containing a Three-Membered Oxide Ring. XXIV. Synthesis of β,β'-Disubstituted Nitriles of Glycidic Acids. B. F. Martynov and A. V. Shchelkunov	3275	3248
Telomerization of Chloroprene in the Reaction with 1,3-Dichlorobutene-2 Under the Action of $FeCl_3$. IV. A. L. Klebanskii, A. G. Saiadian and A. G. Barkhudarian	3279	3253
On the Order of Addition of Lithium to Biphenyl. Iu. P. Egorov, E. P. Kaplan, Z. I. Letina, V. A. Shliapochnikov and A. D. Petrov	3284	3258
Chemistry of Selenophene. XV. 2-Vinylselenophene. Iu. K. Iur'ev, N. N. Mezentsova, and V. E. Vas'kovskii	3288	3262
Decomposition of Lignin by Metallic Sodium in Liquid Ammonia. VII. Chromatographic Investigation of the Phenols Obtained in the Decomposition of Lignin. A. F. Semechkina and N. N. Shorygina	3291	3265
On the Mechanism of Action of Accelerators of the Process of Sulfur Vulcanization. E. I. Tiniakova, E. K. Khrennikova and B. A. Dolgoplosk	3295	3269
Investigations in the Field of the Chemistry of Pyrazolidine. V. On Some Anomalous Reactions of 1,2-Diphenyl-3,5-Dioxopyrazolidine and its Halogen and Thiocyanogen Derivatives. V. G. Pesin, A. M. Khaletskii and Teng Jun-hsiang	3300	3274
Synthesis and Study of the Polymerizability of Halogen-Substituted Styrene Derivatives. VII. Trichlorostyrene and Pentachlorostyrene. N. A. Glukhov, M. M. Koton and Z. A. Koroleva	3303	3277
On the Process of Formation of Polyamide Resins. VIII. The Question of the Alkaline Polymerization of ε-Caprolactam. A. S. Shpital'nyi and N. S. Iablochnik	3307	3282
N-Alkylated and N-Aralkylated Morpholine Derivatives. S. Z. Kaplan, N. M. Grad and A. S. Zvontsova	3310	3285
The Enthalpy of Formation of Compounds of Cadmium with Phosphorus, Arsenic and Antimony. S. A. Shchukarev, M. P. Morozova and M. M. Bortrukova	3315	3289
On the Reactions of Alkyldichlorosilanes with Chlorinated Hydrocarbons. S. N. Borisov, M. G. Voronkov and B. N. Dolgov	3318	3292
Polarography of the Thermal Decomposition of 2,2'-Azobisisobutyronitrile in Vinyl Butyl Ether and Methyl Methacrylate. M. I. Bobrova and A. N. Matveeva-Kudasheva	3323	3297
Preparation of Certain Compounds with Two Isopropenyl Groups. Iu. V. Mitin	3328	3302
Interaction of Cyclopropane Hydrocarbons with Mercuric Salts. VIII. Reaction of γ-Mercurated Alcohols with Zinc Dust. R. Ia. Levina and V. N. Kostin	3332	3307

CONTENTS (continued)

	PAGE	RUSS. PAGE
Synthesis of Polyfunctional Sulfur Compounds from Divinyl Ether and Hydrogen Sulfide. M. F. Shostakovskii, E. S. Shapiro and E. V. Dubrova	3337	3311
From the Field of Organic Insectofungicides. XXXVI. On the Reaction of Tetrachloro- and Pentachlorocyclopentadienes with Certain Unsaturated Compounds. N. N. Mel'nikov and S. D. Volodkovich	3342	3317
Synthesis of Bromo-Substituted β-Phenylethylamines. O. N. Tolkachev, V. G. Voronin and N. A. Preobrazhenskii	3345	3320
Stereochemical Investigations. IV. Schiff Bases from Optically Active α-Benzylethylamine. V. M. Potapov and A. P. Terent'ev	3349	3323
Investigations in the Field of Organocyclosiloxanes. IV. Reactivity of Organocyclosiloxanes in Dependence on the Number of Links in the Cycle. N. N. Sokolov	3354	3328
Investigations in the Naphthalene Series. XVIII. On the Kinetics of Interaction of β-Naphthol with Aqueous Solutions of Ammonia and Ammonium Sulfite. V. V. Kozlov and I. K. Veselovskaia	3359	3333
Synthesis of Certain Derivatives of Adrenalin. II. D,L-Adrenochrome Oxime and Semicarbazone. A. L. Remizov	3364	3338
Derivatives of Bicyclo(1,2,2)Heptane. IV. Some Amines and Aminoalcohols of the Bicyclo(1,2,2)Heptane Series. A. Ia. Khorlin, O. S. Chizhov and N. K. Kochetkov	3370	3345
Author Index for 1958	3377	
Table of Contents for 1958	3409	